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Syntheses, structures, and magnetic properties of heterobimetallic complexes based on tetracyanometallic building blocks

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Abstract

Two tetracyanometalate building blocks, $[Fe(5,5'-dmbipy)(CN)_4]^-$ (2) and $[Fe(4,4'-dmbipy)(CN)_4]^-$ (3) (5,5'-dmbipy = 5,5'-dimethyl-2,2'-bipyridine; 4,4'-dmbipy = 4,4'-dimethyl-2,2'-bipyridine), and two cyano-bridged heterobimetallic complexes, $[Cu_2(bpca)_2-bipyridine)$ $(H_2O)_2Fe_2(5,5'-dmbipy)_2(CN)_8] \cdot 2[Cu(bpca)Fe(5,5'-dmbipy)(CN)_4] \cdot 4H_2O$ (4) and $[Cu(bpca)Fe(4,4'-dmbipy)(CN)_4]_n$ (5) $(bpca = bis(2-b))_2(CN)_4]_n$ (5) $(bpca = bis(2-b))_2(CN)_4]_n$ (7) pyridylcarbonyl)amidate), have been synthesized and structurally characterized. Complex 4 contains two dinuclear and one tetranuclear heterobimetallic clusters in an asymmetric unit whereas the structure of complex 5 features a one-dimensional heterobimetallic zigzag chain. The Cu(II) ion is penta-coordinated in the form of a distorted square-based pyramid. Magnetic studies show ferromagnetic coupling between Cu(II) and Fe(III) ions with g = 2.28, $J_1 = 2.64$ cm⁻¹, $J_2 = 5.40$ cm⁻¹ and TIP = -2.36×10^{-3} for complex 4, and g = 2.17, J = 4.82 cm⁻¹ and zJ' = 0.029 cm⁻¹ for complex 5.

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1. Introduction

The cvano-bridged heterobimetallic assemblies are the continuous interesting topics in the field of molecule-based magnets during the last decades [1-7]. The variety in their structures associated with interesting magnetic properties, such as room temperature magnets [8–11], electrochemically tunable magnets [12,13], photo- and electro-magnetism [14-20], spin crossover materials [21–24], single-molecule magnets [25-34] and single-chain magnets [7,35-38], is at the main origin of the importance in these compounds. One of the synthetic approaches for low-dimensional heterometallic

cvano-bridged complexes is from the reaction of hexacvanometallates and partially blocked transition metal ions with organic polydentate ligands [3,4,39–43]. Recently, synthetic strategies to prepare cyano-bridged heterobimetallic systems by using modified cyanometalates $([M(L)_{\nu}(CN)_{x}]^{(x-m)-})$ as multidentate ligands were developed. The following are some typical examples: $[M(L)(CN)_4]^ (M = Cr^{3+}, Fe^{3+},$ L = 1,10-phenanthroline; or 2,2'-bipyridine or 2-aminomethylpyridine) [44–50], [(tacn) $M(CN)_3$] (M = Co³⁺, Cr³⁺; tacn = 1,4,7-triazacyclononane) and [(Me₃tacn)M(CN)₃] $(M = Cr^{3+}, Mo^{3+}; Me_3tacn = N, N', N''-trimethyl-1, 4, 7-tri$ azacyclononane) [51–55], [(tach)M(CN)₃] ($M = Cr^{3+}$, Fe^{3+} , Co^{3+} ; tach = 1,3,5-triaminocyclohexane) [56], [(Tp)Fe $(CN)_3$ ⁻ (Tp = hydrotris(pyrazolyl)borate and its derivatives) [30-34,37,57-62], $[Fe(bpca)(CN)_3]^-$ (bpca = bis(2pyridylcarbonyl)amidate) [63,64] and $[Cp^*M(CN)_3]^ (M = Co^{3+})$, Cp = cyclopentadienyl; $M = Rh^{3+}$, Ir^{3+} , $Cp^* = 1,2,3,4,5$ -pentamethylcyclopentadienyl) [65–68]. On

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the basis of these building blocks, some heterobimetallic complexes exhibiting interesting structures and magnetic properties were synthesized [44–69], including several single-molecule magnets (SMMs) [25,29-34] and single-chain magnets (SCMs) [35–38]. To further investigate the structure and magnetic properties of low-dimensional heterobimetallic complexes based on the versatile building block of [M(L)(CN)₄]⁻, we synthesized two building blocks, [Fe- $(5,5'-dmbipy)(CN)_4$ ⁻ (2), [Fe(4,4'-dmbipy)(CN)_4]⁻ (3) (4,4'-dmbipy = 4,4'-dimethyl-2,2'-bipyridine, 5,5'-dmbipy =5.5'-dimethyl-2.2'-bipyridine). The structure of **3** has been reported briefly in a recent review [7]. Based on the above two new tetracyanometalate building blocks, two novel cyano-bridged heterobimetallic assemblies were synthesized, namely, $[Cu_2(bpca)_2(H_2O)_2Fe_2(5,5'-dmbipy)_2(CN)_8] \cdot 2[Cu$ (bpca) $Fe(5,5'-dmbipy)(CN)_4] \cdot 4H_2O$ (4) and [Cu(bpca) $Fe(4,4'-dmbipy)(CN)_4]_n$ (5) (bpca = bis(2-pyridylcarbonyl) amidate). Herein, their structures and magnetic properties are presented.

2. Experimental

2.1. Reagents

All chemicals were of reagent grade and used as received. 4,4'-dimethyl-2,2'-bipyridine, 5,5'-dimethyl-2,2'-bipyridine, and 1,3,5-tris(2-pyridyl) triazine were purchased from the Aldrich Chemicals Company. Hbpca was prepared according to the literature method [70].

Caution! While no problems were encountered in this work, the perchlorate salts are potentially explosive and cyanides are very toxic. Thus, these starting materials should be handled in small quantities and with great caution.

2.2. Preparation of $K_2[Fe(5,5'-dmbipy)(CN)_4] \cdot 3H_2O(1)$

Complex 1 was synthesized by the modification of a literature method [71]. 2.76 g (0.015 mol) of 5,5'-dimethyl-2,2'-bipyridine and 2.0 g (0.05 mol) of ferrous ammonium sulfate hexahydrate were dissolved in 200 mL of distilled water. The mixture was heated to slightly below the boiling point under stirring. KCN (5.0 g) in 10 mL of water was added all at once to the hot solution. After the solution was stirred for 1 h, 200 mL of the aqueous solution containing 25 g of KCN was added to the dark red solution. The mixture was heated for 24 h at 120 °C with continuous stirring. After cooling and filtration to remove the small fraction of insoluble material, the filtrate was heated at 110 °C to vaporize the water until the volume of solution was left approximately 100 mL. After a few hours of cooling and aging, the dark red crystalline product was isolated by filtration, washed with diethyl ether, and dried under vacuum at room temperature. Recrystallization in methanol afforded violet-red crystals, K₂[Fe(5,5'-dmbi $py)(CN)_4] \cdot 3H_2O$ (1). Yield: 83%. Anal. Calc. for C₁₆H₁₈N₆O₃K₂Fe: C, 40.33; H, 3.78; N, 17.64. Found: C, 40.60; H, 3.82; N, 17.46%. IR (KBr, cm⁻¹): 2033 ($v_{C=N}$).

2.3. Preparation of $(Ph_4P)[Fe(5,5'-dmbipy)(CN)_4]$ (2)

Chlorine gas was bubbled through a dark red aqueous solution (100 mL) of $K_2[Fe(5,5'-dmbipy)(CN)_4] \cdot 3H_2O$ (1.9 g, 4 mmol) for 10 min. under continuous stirring at room temperature. A color change from red to orangered was observed, and the small fraction of insoluble material was removed by filtration. The addition of a concentrated aqueous solution (10 mL) of tetraphenylphosphonium chloride (8 mmol, 3.00 g) caused the precipitation of complex 2 as an orange solid, which was recrystallized in acetonitrile to afford X-ray-quality orange crystals, (Ph₄P)[Fe(5,5'-dmbipy)(CN)₄]. Yield: 2.0 g, 70%. Anal. Calc. for C₄₀H₃₂FeN₆P: C, 70.22; H, 4.68; N, 12.29. Found: C, 70.35; H, 4.57; N, 12.17%. IR (KBr, cm⁻¹): 2123 ($v_{C=N}$). The tetrabutylammonium salt of 2 was also prepared by the addition of a concentrated aqueous solution of tetrabutylammonium chloride.

2.4. Preparation of $(Ph_4P)[Fe(4,4'-dmbipy)(CN)_4] \cdot H_2O$ (3)

Complex **3** was prepared as described for **2** except 4,4'dimethyl-2,2'-bipyridine was used instead of 5,5'dimethyl-2,2'-bipyridine. Yield: 71%. Recrystallization of tetraphenylphosphonium salt of **3** in acetonitrile afforded X-ray-quality orange crystals, $(Ph_4P)[Fe(4,4'-dmbi$ $py)(CN)_4] \cdot H_2O$. *Anal.* Calc. for $C_{40}H_{34}FeN_6OP$: C, 68.42; H, 4.85; N, 11.97. Found: C, 68.05; H, 4.77; N, 11.65%. IR (KBr, cm⁻¹): 2122 ($\nu_{C=N}$). The tetrabutylammonium salt of **3** was also prepared by the addition of a concentrated aqueous solution of tetrabutylammonium chloride.

2.5. Preparation of $[Cu_2(bpca)_2(H_2O)_2Fe_2(5,5'-dmbipy)_2-(CN)_8] \cdot 2[Cu(bpca)Fe(5,5'-dmbipy)(CN)_4] \cdot 4H_2O$ (4)

A solution containing $Cu(ClO_4)_2 \cdot 6H_2O$ (18.6 mg, 0.05 mmol) and Hbpca (11.4 mg, 0.05 mmol) in water (2 mL) was added to the glass tube, and a mixture of methanol and water (20 mL, methanol/water (v/v) = 4:1) was gently added as an upper layer. A solution of (Bu₄N)[Fe(5,5'-dmbipy)(CN)₄] (30 mg, 0.05 mmol) in methanol (2 mL) was added carefully as a third layer, and then the tube sealed. Complex **4** was obtained as blue-black needle-shaped crystals after several weeks. The resulting crystals were filtered and washed with H₂O and MeOH. Yield: 43%. *Anal.* Calc. for C₁₁₂H₉₂Cu₄Fe₄N₃₆O₁₄: C, 50.88; H, 3.48; N, 19.07. Found: C, 51.29; H, 3.54; N, 19.39%. IR (KBr, cm⁻¹): 2130, 2157 ($v_{C=N}$).

2.6. Preparation of $[Cu(bpca)Fe(4,4'-dmbipy)(CN)_4]_n$ (5)

Complex 5 was prepared as described for 4 except $(Bu_4N)[Fe(4,4'-dmbipy)(CN)_4] \cdot H_2O$ was used instead of $(Bu_4N)[Fe(5,5'-dmbipy)(CN)_4]$. Complex 5 was obtained as blue-black needle-shaped crystals. Yield: 43%. Anal.

Calc. for $C_{28}H_{20}CuFeN_9O_2$: C, 53.05; H, 3.15; N, 19.88. Found: C, 53.29; H, 3.24; N, 19.79%. IR (KBr, cm⁻¹): 2129, 2181 ($\nu_{C=N}$).

2.7. Physical measurements

Elemental analyses for C, H and N were performed on a Perkin–Elmer 240C analyzer. Infrared spectra were recorded on a Vector22 Bruker spectrophotometer with KBr pellets in the 400–4000 cm⁻¹ region. The magnetic susceptibility measurements of the polycrystalline samples were measured over the temperature range of 1.8– 300 K with a Quantum Design MPMS-XL7 SQUID magnetometer using an applied magnetic field from 100 to 2000 Oe. Field dependences of magnetization were measured using a flux magnetometer in an applied field up to 70 kOe.

2.8. X-ray crystallography measurements of complexes 2-5

The crystal structures of complexes 2–5 were determined on a Bruker SMART CCD diffractometer using monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS supplied by Bruker. Structures were solved by direct methods using the program SHELXTL-97. The positions of the metal atoms and their first coordination spheres were located from direct methods *E*maps; other non-hydrogen atoms were found using alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, were refined anisotropically. Hydrogen atoms were placed in calculated position

Table 1 Crystallographic data for complexes **2–5** and refined as riding atoms with a uniform value of U_{iso} . A summary of the crystal data collection and refinement parameters for complexes 2–5 is given in Table 1.

3. Results and discussion

3.1. Syntheses and spectroscopic studies

In an effort to continue the remarkably diverse chemistry starting from a tailored cyanometalate precursor, we explored the synthesis and use of the building blocks with low-spin iron(III) ions, $[Fe(5,5'-dmbipy)(CN)_4]^-$ (2) and $[Fe(4,4'-dmbipy)(CN)_4]^-$ (3). The complexes, $[Fe(bipy)-(CN)_4]^-$ and $[Fe(phen)(CN)_4]^-$ were synthesized early in the 1960s [71], but the crystal structures were not determined until 2002 [44,45]. Complexes 2 and 3 were synthesized by a modified literature method [71]. The yield is relatively high and the synthetic work-up is simple. The paramagnetic result of magnetic measurements and the cyanide stretching frequency at 2123 and 2122 cm⁻¹ demonstrate the low-spin character of the iron(III) in 2 and 3.

Based on the new building blocks, $[Fe(4,4'-dmbipy)(CN)_4]^-$ and $[Fe(5,5'-dmbipy)(CN)_4]^-$, after the reactions with the partially blocked copper(II) complex $[Cu(bpca)]^+$, two novel cyano-bridged heterometallic assemblies were synthesized. The IR absorptions for bridging and terminal cyanide ligands occur at 2157 and 2130 cm⁻¹ for complex **4**, and at 2129 and 2181 cm⁻¹ for complex **5**, respectively. The products differ very dramatically by using different tetracyanometalate building blocks.

	2	3	4	5
Empirical formula	C ₄₀ H ₃₂ FeN ₆ P	C40H34FeN6OP	C ₁₁₂ H ₉₂ Cu ₄ Fe ₄ N ₃₆ O ₁₄	C ₂₈ H ₂₀ CuFeN ₉ O ₂
Formula weight	683.54	701.55	2643.78	633.92
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1/c$	Pbcn	$P\bar{1}$	$P2_1/n$
a (Å)	9.2930(9)	22.805(5)	8.934 (2)	6.8414 (14)
b (Å)	24.980(5)	18.797(4)	14.745(4)	30.770(6)
c (Å)	14.904(3)	16.504(4)	24.065(6)	13.349(3)
α (°)	90	90	74.612(2)	90
β (°)	94.29(3)	90	81.973(4)	103.68(3)
γ (°)	90	90	75.591(4)	90
$V(\text{\AA}^3)$	3447.7(12)	7074(4)	2951.0(12)	2730.5(10)
Ζ	4	8	1	4
ρ (calc) (g cm ⁻³)	1.317	1.317	1.488	1.542
$T(\mathbf{K})$	293(2)	293(2)	293(2)	293(2)
$\mu (\mathrm{mm}^{-1})$	0.522	0.512	1.260	1.354
<i>F</i> (000)	1420	2900	1348	1288
Index ranges	$0 \leq h \leq 11$,	$-21 \leq h \leq 30$,	$-10 \leqslant h \leqslant 11$,	$-8 \leqslant h \leqslant 8$,
	$0 \leq k \leq 29$,	$-24 \leqslant k \leqslant 24$,	$-17 \leqslant k \leqslant 18$,	$-37 \leqslant k \leqslant 37$,
	$-17 \leq l \leq 17$	$-20 \leqslant l \leqslant 21$	$-18 \leqslant l \leqslant 29$	$-14 \leq l \leq 16$
Data/restraints/parameters	6702/0/435	8484/0/444	11 282/0/797	5375/0/372
Goodness-of-fit (F^2)	1.020	0.908	1.086	0.977
$R_1^{a}, wR_2^{b} (I > 2\sigma(I))$	0.0489, 0.1219	0.0550, 0.1139	0.0631, 0.1238	0.0562, 0.0935
R_1^{a} , wR_2^{b} (all data)	0.1578, 0.1561	0.1085, 0.1289	0.0933, 0.1290	0.1030, 0.1004
Largest differences in peak and hole (e $Å^{-3}$)	0.367 and -0.293	0.585 and -0.363	0.542 and -0.601	0.486 and -0.569

If using the parent unsubstituted bipyridine compound $[Fe(bpy)(CN)_4]^-$, the final product is the neutral heterodinuclear species, { $[Fe(bipy)(CN)_4][Cu(bpca)(H_2O)]$ } [7].

3.2. Crystal structures

The structures of complexes 2 and 3 feature mononuclear [Fe(5,5'-dmbipy)(CN)₄]⁻ or [Fe(4,4'-dmbipy)(CN)₄]⁻ anions, respectively (Fig. 1). The iron(III) ions in both complexes are coordinated by two nitrogen atoms from 2.2-bipyridine derivatives and four cyanide carbon atoms, taking a distorted octahedral geometry. The small bond angle $(N(1)-Fe(1)-N(2), 80.66(15)^{\circ}$ for 2, $80.61(19)^{\circ}$ for 3) around Fe(1) with chelating bipy is one of the main factors accounting for this distortion. The Fe(1)-N(bipy)bond distances in 2 and 3 (1.980-2.004 Å) are almost the same as those found in the low-spin iron(III) compound of $[Fe^{III}(bipy)(CN)_4]^-$ (1.987–2.003 Å). Good agreement is observed between the Fe(1)-C(cvano) bond distances of 2 and 3 (1.900–1.972 Å) and those reported for cyanocontaining mononuclear low-spin iron(III) complexes. The bipy ligand is almost planar. The bond angles of Fe-C≡N range from 177.0 to 178.3°. The selected bond lengths and angles for complexes 2-5 are given in Tables 2 and 3.

The crystal structure measurements show that **4** is a cocrystallized compound with two dinuclear and one tetranuclear heterobimetallic clusters in an asymmetric unit (Fig. 2). The dinuclear cluster is a neutral cyano-bridged dimer. The $[(bpca)Cu(H_2O)]^+$ unit is linked to the $[Fe(5,5'-dmbipy)(CN)_4]^-$ unit by one cyanide group with Cu(2)-N(15) bond distance of 1.945(3) Å. The tetranuclear cluster is a neutral cyano-bridged compound of square. Within the square, each $[(bpca)Cu]^+$ unit is linked to two $[Fe(5,5'-dmbipy)(CN)_4]^-$ units by two cyanide groups at*cis*-position. The Cu^{II} ion is penta-coordinated in the form of a distorted square-based pyramid. Three nitrogen atoms from a bpca ligand and a nitrogen atom from a cyanide group of $[Fe(5,5'-dmbipy)(CN)_4]^-$ form the equatorial plane with bond distances of 1.947(3)–2.026(3) Å, and the

Table 2 Selected bond lengths (Å) and angles (°) for complexes 2 and 3

2		3	
Bond distances			
Fe(1)-C(13)	1.931(5)	Fe(1)-C(1)	1.910(3)
Fe(1)-C(14)	1.922(5)	Fe(1)-C(2)	1.918(3)
Fe(1)-C(15)	1.966(5)	Fe(1)-C(3)	1.949(3)
Fe(1)-C(16)	1.972(5)	Fe(1)-C(4)	1.949(3)
Fe(1) - N(1)	2.004(3)	Fe(1)-N(1)	1.986(2)
Fe(1)-N(2)	1.910(3)	Fe(1) - N(2)	1.980(2)
Bond angles			
N(1)-Fe(1)-N(2)	80.66(15)	N(1)-Fe(1)-N(2)	80.61(9)
N(1)-Fe(1)-C(13)	96.59(16)	N(1)-Fe(1)-C(1)	98.50(10)
N(2)-Fe(1)-C(14)	95.93(17)	N(2)-Fe(1)-C(2)	94.90(10)
C(13)-Fe(1)-C(15)	90.76(19)	C(1)-Fe(1)-C(2)	86.28(11)
N(1)-Fe(1)-C(15)	90.75(1)	N(1)-Fe(1)-C(3)	88.40(10)
N(2)-Fe(1)-C(16)	89.56(1)	N(2)-Fe(1)-C(4)	86.29(9)

apical position is occupied by one nitrogen atom from a cyanide group of another $[Fe(5,5'-dmbipy)(CN)_4]^-$ (Cu(1)-N(5), 2.313 Å). The Fe^{III} ion has a distorted octahedral geometry, completed by two nitrogen atoms from a 5,5'-dmbipy ligand and four carbon atoms from the cyanide groups. The square is slightly distorted, as reflected in the bond angles of C(15)-Fe(1)-C(16) [86.41(16)°] and N(5)-Cu(1)-N(9)^{#1} (91.25(13)°; #1: -x + 1, -y, -z + 1). The plane made up of the bpca ligand and Cu(II) (N(8), C(23), N(7), C(22), N(6), Cu(1)) is almost perpendicular to the plane made up of 5,5'-dmbipy ligand and Fe(III) (N(1), C(6), C(7), N(2), Fe(1)).

Different from complex 4, the structure of complex 5 consists of $Fe(4,4'-dmbipy)(CN)_4Cu(bpca)$ unit which forms a neutral one-dimensional zigzag chain (Fig. 3). Within the chain, the Cu^{II} ion is penta-coordinated in the form of a distorted square-based pyramid. Three nitrogen atoms from the bpca ligand and a nitrogen atom from a cyanide group of $[Fe(4,4'-dmbipy)(CN)_4]^-$ form the equatorial plane with bond distances of 2.097–2.234 Å (Cu–N), and the apical position is occupied by one nitrogen atom from a cyanide group of another $[Fe(4,4'-dmbipy)(CN)_4]^-$ unit with a bond length of 2.036 Å



[Fe(5, 5'-dmbipy)(CN)₄]⁻

[Fe(4, 4'-dmbipy)(CN)₄]⁻

Fig. 1. ORTEP representation of the anion building blocks in complexes 2 and 3. The thermal ellipsoids are drawn at 30% probability.



Fig. 2. ORTEP representation of the selected unit of complex 4. The thermal ellipsoids are drawn at 30% probability. Symmetry code for the generated atoms: (a) 1 - x, -y, 1 - z.

Table 3 Selected bond lengths (Å) and angles (°) for complexes ${\bm 4}$ and ${\bm 5}^a$

4		5	
Bond distances			
Cu(1)–N(5)	2.313(3)	Cu(1) - N(1)	2.097(3)
Cu(1)–N(6)	1.999(4)	Cu(1)–N(9)	2.100(3)
Cu(1)–N(7)	1.947(3)	Cu(1)-N(7)	2.205(3)
Cu(1)–N(8)	2.026(3)	Cu(1)–N(8)	2.234(3)
Cu(1)-N(9)#1	1.953(3)	Cu(1)-N(2)#2	2.036(3)
Cu(2)–N(15)	1.945(3)	Fe(1)-C(1)	1.911(4)
Cu(2)–O(5)	2.311(2)	Fe(1)-C(3)	1.900(4)
Fe(1)-C(16)	1.911(4)	C(1)-N(1)	1.172(4)
Fe(1)-C(15)	1.900(4)	C(3)–N(3)	1.179(4)
C(16)–N(5)	1.147(4)		
C(13)–N(3)	1.140(3)		
Bond angles			
N(5)-Cu(1)-N(6)	96.13(13)	N(2)#2-Cu(1)-N(1)	95.80(13)
N(5)-Cu(1)-N(7)	93.12(13)	N(2)#2-Cu(1)-N(9)	132.26(12)
N(5)-Cu(1)-N(8)	97.59(13)	N(2)#2-Cu(1)-N(7)	93.33(11)
N(5)-Cu(1)-N(9)#1	91.25(13)	N(2)#2-Cu(1)-N(8)	103.19(12)
C(15)-Fe(1)-C(16)	86.41(16)	C(1)-Fe(1)-C(3)	97.74(16)
C(15)-Fe(1)-N(1)	178.62(12)	C(2)-Fe(1)-C(3)	83.44(15)
C(16)-Fe(1)-N(2)	176.32(11)	C(3)-Fe(1)-N(5)	87.17(14)
Fe(1)-C(16)-N(5)	178.4(3)	C(3)-Fe(1)-N(6)	93.10(14)
Fe(1)-C(14)-N(4)	176.7(3)	Fe(1)-C(1)-N(1)	178.5(3)
Cu(2)–N(4)–C(41)	177.2(4)		



^a Symmetry transformation used to generate equivalent atoms: #1 -x + 1, -y, -z + 1; #2 x + 1, y, z.

 $(Cu(1)-N(2)^{\#2}; \#2: x + 1, y, z)$. The plane made up of the bpca ligand and Cu(II) (N(8), C(23), N(9), C(22), N(7),Cu(1)) is almost perpendicular to the plane made up of 4,4'-dmbipy ligand and Fe(III) (N(5), C(5), C(10), N(6), Fe(1)). The pyridine ring of the bpca ligands from adjacent chains in the crystal exhibits a quasi-parallel (dihedral angle 3.0°) stacking along the *a*-axis, and the shorter interchain pyridine–pyridine interplanar separation (*ca.* 3.580 Å) indicates that there are weak interchain π - π stacking interactions.

Fig. 3. Top: ORTEP representation of the selected unit of complex 5. The thermal ellipsoids are drawn at 30% probability. Symmetry code for the generated atoms: (a) 1 + x, y, z. Bottom: view of the 1D chain structure of 5 along the *a*-axis. The hydrogen atoms are omitted for clarity.

3.3. Magnetic properties

Magnetic measurements for complexes 4 and 5 were performed on polycrystalline samples in the temperature range of 1.8–300 K. The temperature dependence of susceptibility for **4** in the forms of $\chi_{\rm M}$ and $\chi_{\rm M}T$ versus *T* at 2 kOe is shown in Fig. 4. The value of $\chi_{\rm M}T$ at room temperature is 3.30 emu K mol⁻¹, which is slightly higher than the spin-only value of 3.20 emu K mol⁻¹ based on the Fe₄Cu₄ unit ($g_{\rm Fe} = g_{\rm Cu} = 2.1$, $S_{\rm Fe} = S_{\rm Cu} = 1/2$). As the temperature decreases, $\chi_{\rm M}T$ gradually increases and reaches 4.50 emu K mol⁻¹ at 25 K, and then it abruptly increases reaching 5.40 emu K mol⁻¹ at 1.8 K, indicating the ferromagnetic coupling between the Cu^{II} and Fe^{III} ions, which is further confirmed by the nearly saturated magnetization value of $8.46N\beta$ mol⁻¹ under the 70 kOe magnetic field at 1.8 K (Fig. 5). According to the structure, the Hamiltonian of **4** can be described as $\hat{H} = -2J_1[\hat{S}_{\rm Fe1}(\hat{S}_{\rm Cu1} + \hat{S}_{\rm Cu1A}) + \hat{S}_{\rm Fe1A}(\hat{S}_{\rm Cu1} + \hat{S}_{\rm Cu1A})] - 2 \times 2J_2\hat{S}_{\rm Fe2}\hat{S}_{\rm Cu2}$, where J_1 and J_2 are the coupling constants mediated by cyanide in tetranuclear Fe₂Cu₂ cluster and dinuclear FeCu cluster, respec-



Fig. 4. Temperature dependence of $\chi_M T$ for complex 4 at 2000 Oe. The solid line represents the best-fit to the data. Inset: temperature dependence of χ_M for complex 4.



Fig. 5. Field dependence of the magnetization for complex 4 at 1.8 K. The solid line is a guide for the eyes.

tively. Thus, the Van Vleck expression can be written as follows when TIP is taken into account:

$$\chi_{\rm M} = \frac{2Ng^2\beta^2}{kT} \left(\frac{2 + e^{-2J_1/kT} + 5e^{2J_1/kT}}{7 + e^{-4J_1/kT} + 3e^{-2J_1/kT} + 5e^{2J_1/kT}} + \frac{2}{3 + e^{-2J_2/kT}} \right) + \text{TIP}$$
(1)

The best fit between 12 and 300 K gives the parameters: g = 2.28, $J_1 = 2.64 \text{ cm}^{-1}$, $J_2 = 5.40 \text{ cm}^{-1}$ and TIP = -2.36×10^{-3} with $R = \sum \left[(\chi_M T)_{calcd} - (\chi_M T) \text{obsd} \right]^2 / \sum (\chi_M T)_{obsd}^2 = 9.2 \times 10^{-4}$. This result indicates that the cyanide ligand mediates the ferromagnetic coupling between the Cu^{II} and Fe^{III} ions.

The temperature dependence of susceptibility at 2 kOe for **5** is shown in Fig. 6. The $\chi_{\rm M}T$ value at room temperature is 0.93 emu K mol⁻¹, and it goes up in a mild way in the temperature range of 10–300 K, followed by a sharp increase with 3.35 emu K mol⁻¹ at 1.8 K, suggesting the ferromagnetic coupling between the Fe^{III} and Cu^{II} ions. The field dependence of magnetization was measured at 1.8 K (Fig. 7). The magnetization gradually increases with the applied field and reaches a value of $1.79N\beta$ mol⁻¹ at 70 kOe, which is lower than the theoretical value of $2.10N\beta$ mol⁻¹ based on the CuFe unit $(2.1 \times 1/2 + 2.1 \times 1/2)$ with ferromagnetic coupling between the Fe^{III} and Cu^{II} ions, indicating that the magnetization does not reach saturation at this field. According to the structure, complex **5** can be regarded as a one-dimensional uniform chain $(\hat{H} = -J\sum_{i=1}^{n-1} \hat{S}_{A_i} \cdot \hat{S}_{A_{i+1}})$ [72]. When the intermolecular interaction (zj') is taken into account, the van Vleck formula is written as

$$\chi_{\rm chain} = \frac{Ng^2\beta^2}{4kT} \left[\frac{N}{D}\right]^{2/3} \tag{2}$$

$$\chi_{\rm M} = \frac{\chi_{\rm chain}}{1 - (2zj'/Ng^2\beta^2)\chi_{\rm chain}} \tag{3}$$



Fig. 6. Temperature dependence of $\chi_M T$ for complex 5 at 2000 Oe. The solid line represents the best-fit to the data. Inset: temperature dependence of χ_M for complex 5.



Fig. 7. Field dependence of the magnetization for complex **5** at 1.8 K. The solid line is a guide for the eyes.

where

$$\begin{split} N &= 1.0 + 5.79799y + 16.902653y_2 + 29.376885y_3 \\ &+ 29.832959y_4 + 14.036918y_5 \\ D &= 1.0 + 2.7979916y + 7.0086780y_2 + 8.6538644y_3 \\ &+ 4.5743114y_4 \\ y &= J/2kT \end{split}$$

The best fit by least squares gives the parameters: g = 2.17, $J = 4.82 \text{ cm}^{-1}$ and $zJ' = 0.029 \text{ cm}^{-1}$ with $R = 4.0 \times 10^{-4}$, indicating the existence of ferromagnetic interaction. The AC susceptibility studies carried out in a 5 Oe oscillating field with frequencies up to 1500 Hz for 5 showed no evidence for slow paramagnetic relaxation, suggesting that complex 5 is not a single-chain magnet.

In summary, two new tetracyanide-containing building blocks 2 and 3 were synthesized and characterized. The incorporations of 2 and 3 with partially blocked salt $[Cu(bpca)]^{2+}$ afford compound (4) consisting of dimeric FeCu and tetrameric Fe₂Cu₂, and a zigzag chain (5). Magnetic properties studies show ferromagnetic coupling between Cu(II) and Fe(III) ions with g = 2.28, $J_1 = 2.64$ cm⁻¹ and $J_2 = 5.40$ cm⁻¹ for 4, and g = 2.17, J = 4.82 cm⁻¹ and zJ' = 0.029 cm⁻¹ for 5. The present results suggest that the mononuclear compounds 2 and 3 are the possible building blocks for assembling new cyanide-bridged heterometallic high-spin clusters and lowdimensional polymers with interesting magnetic properties.

4. Supplementary material

CCDC 663215, 663216, 663217, and 663218 contain the supplementary crystallographic data for this paper. These 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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