Synthesis, structures and single chain magnet behavior of a cyano-bridged {Fe$_2$Cu} chain

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ABSTRACT

The reaction of tricyanometallate precursor, (Bu$_4$N)[(pzTp)Fe(CN)$_3$] (pzTp = tetrakis(pyrazolyl)borate) with Cu(ClO$_4$)$_2$·6H$_2$O in the presence of the monodentate 4-styrylpyridine ligand afford one novel one-dimensional (1D) heterobimetallic cyano-bridged chain, [Fe(pzTp)(CN)$_3$]$_2$Cu(4-styrylpyridine)$_2$•2H$_2$O•4CH$_3$OH (**1**). The molecular structure was determined by single-crystal X-ray diffraction. In compound **1**, the Fe^{III} ion is coordinated by three cyanide carbon atoms and three nitrogen atoms of pzTp anions. Whereas, the Cu^{II} ion is surrounded by four cyanide nitrogen atoms and two nitrogen atoms from two monodentate 4-styrylpyridine ligands. Magnetic measurements indicate that compound **1** exhibits intrachain ferromagnetic coupling and single-chain magnets behavior.

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Recently, molecule-based materials exhibits exciting interesting magnetic behaviors that include magnetic ordering with ordering/critical temperatures (T_c) exceeding room temperature, single molecule/chain quantum effects, switchable magnetic state *via* photo, thermal, pressure etc [1–5]. The discovery of single-molecule magnets (SMMs) enables the storage of information at the molecular and nanoscale level, which may be used in molecular devices and quantum computer science [6,7].

Analogous to SMMs, single-chain magnets (SCMs) are composed of magnetically isolated chains for which a finite magnetization can be frozen in the absence of an applied magnetic field [8]. For SCMs large uniaxial magnetic anisotropy is a must, and the inevitable interchain interactions should be much weaker than intrachain interactions. And the relaxation of the magnetization becomes very slow at low temperature such that these systems can then be considered to be real magnets [9,10].

Cyanometallate precursors offer a number of distinct advantages for the design of molecular magnets. An alternative synthetic strategy is to use building blocks of modified cyanometalates [LMA(CN)$_x$]$^{n-}$ (L = ligand, M, A = metal ion, x = 2 dicyano, 3 tricyano, 4 tetracyano; n = 0, 1, 2) [11–14]. On the basis of these building blocks, some heterobimetallic complexes exhibiting interesting magnetic properties were synthesized, including single-molecule magnets and single-chain magnets. Among them, we note the ability of the tricyanometalate to link various metal ions, leading to a wide diversity of structural architectures ranging from discrete polynuclear complexes to various 1D assemblies [15]. Some of them are promising cyano-bridged SMMs and SCMs.

To enhance the steric effect and decrease the interchain interaction, the bulky monodentate 4-styrylpyridine ligand was used to occupy the apical positions of the Cu^{II} ions instead of solvent molecules, which prevents the through bond magnetic interactions between the chains. The tailored cyanometalate precursor, bulky [Fe(pzTp)(CN)$_3$]$^-$, have been chosen as our main building block instead of [Fe(Tp)(CN)$_3$]$^-$ (Tp = Tris(pyrazolyl)hydroborate) units to increase the metal ion distances of the neighboring chains. In comparison to those precursors reported before [15], the building block is sterically more demanding and bears a negative charge. Herein, we report the synthesis, crystal structures, and magnetic properties of one 1D cyano-bridged heterobimetallic chain complex, [Fe(pzTp)(CN)$_3$]$_2$Cu(4-styrylpyridine)$_2$•2H$_2$O•4CH$_3$OH (**1**). Compound **1** exhibits single-chain magnet behavior and slow magnetic relaxation by using bulky 4-styrylpyridine monodentate ligand.

Compound **1** was synthesized by a diffusion method in a test tube [16]. A mixed methanol solution of Bu$_4$N[Fe(pzTp)(CN)$_3$] and 4-styrylpyridine was slowly layered over an aqueous solution of Cu(ClO$_4$)$_2$•6H$_2$O. Crystallization required several weeks. Single-crystal X-ray diffraction analysis [17] revealed that **1** crystallizes in a P−1 space group. The crystal structure comprises neutral bimetallic double-zigzag [Fe(pzTp)(CN)$_3$]$_2$Cu(4-styrylpyridine)$_2$ chains with uncoordinated water and methanol molecules located between them (Fig. 1). In the neutral chain, the [Fe(pzTp)(CN)$_3$]$^-$ unit bridged two Cu^{II} ions through two of its three cyanide groups in the *cis* position, whereas each Cu^{II} coordinated to four nitrogen atoms from the CN$^-$ bridges. Dihedral angles of 57° were formed between the planes of the triangular Fe$_2$Cu unit owing to the steric effect of the bulky [Fe(pzTp)(CN)$_3$]$^-$ building block.

The crystal structure consisted of two unique iron and one copper centers. Each iron center was located in an octahedral environment

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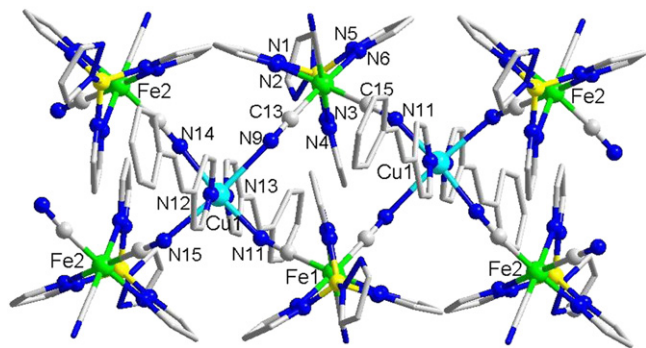*E-mail addresses:* liutao@dlut.edu.cn (T. Liu), cyduan@dlut.edu.cn (C.-Y. Duan).

Fig. 1. Side view of a 1-D double-zigzag chain along the *c*-axis. H atoms have been omitted for clarity. Atomic scheme: Fe, bright green; Cu, turquoise; C, gray; N, blue; B, yellow.
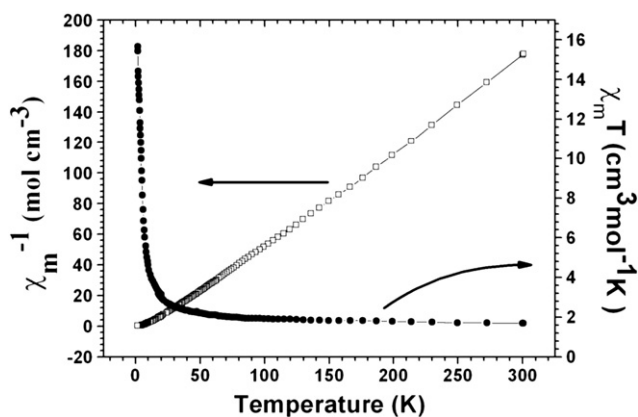

Fig. 2. Thermal variation of magnetic susceptibility, $\chi_{m}T$ *vs* T (●) and χ_{m}^{-1} *vs* T (□) of compound **1** under an applied field of 1 kOe in the temperature range of 2–300 K.

with three nitrogen atoms from the pzTp units and three cyanide carbon atoms. The equatorial plane of the copper center was occupied by four cyanide nitrogen atoms, and two nitrogen atoms from 4-styrylpyridine occupied its apical positions, providing an N_6 coordination sphere. The Cu—$N_{equatorial}$ bond distances were 2.018(4)–2.481(5) Å and the Cu—N_{apical} bond distances were 2.001(4) Å and 2.019(4) Å for Cu1, which are in good agreement with those observed previously in related compounds [18]. The Fe—C bond distances were 1.912(5)–1.919(6) Å and 1.898(6)–1.917(6) Å and the Fe—N bond distances were 1.968(4)–1.970(4) Å and 1.959(4)–1.973(4) Å for Fe1 and Fe2, respectively (Table 1). The shortest interchain metal–metal distance was 10.1 Å. Such a large distance will diminish the interchain magnetic interactions, substantiating the potential for single-chain magnet behavior without magnetic ordering. The pyrazolyl rings of the pzTp ligands from adjacent chains (symmetry:

$2 - x$, $1 - y$, -z) are parallel to each other, and the shorter interchain pyrazolyl separation (3.671 Å) indicates that there exist weak interchain π–π stacking interactions from parallel quasi-eclipsed stacking pyrazolyl rings along the *a* axis [19].

The temperature dependence of the $\chi_{m}T$ product and inverse magnetic susceptibility ($1/\chi_{m}$) for compound **1** at 1000 Oe in the temperature range 2–300 K [20]. On decreasing temperature, $\chi_{m}T$ increases gradually from the room-temperature value of 1.69 cm^3mol^{-1} K, which is higher than the spin-only value of 1.125 cm^3mol^{-1} K per Fe_2Cu unit (Fig. 2). The $\chi_{m}T$ value gradually increased to a broad maximum of 15.70 cm^3mol^{-1} K around 2 K. This behavior indicates the dominant ferromagnetic (FM) interaction [21,22]. The magnetic susceptibility data above 40 K were fitted by the Curie–Weiss law, which gave a Curie constant of 1.64 cm^3mol^{-1} K and a Weiss temperature of 13.52 K. The positive Weiss temperature confirms the dominant FM interactions in the temperature region. At 2 K, the isothermal magnetization increased steeply with the applied magnetic field and reached a value of 3.38 Nβ at 70 kOe (Fig. 3), is slightly higher than the predicted saturation value (3.0 Nβ for two Fe(III) and one Cu(II) assuming g = 2.00), which confirms the intrachain FM interactions.

To probe the dynamics of the magnetization relaxation of **1**, ac magnetic measurements were performed in a 3.5 Oe ac field oscillating at 1–1000 Hz. There are obvious peaks in the χ'' data between 2 and 4 K, and move to higher frequency with increasing temperature (Fig. 4), precluding a three-dimensional (3D) ordering. The shift of

Table 1
Selected bond lengths (Å) and angles (°) for compound **1**.

Compound **1**			
Cu(1)–N(13)	2.001 (4)	Fe(1)–N(2)	1.968 (4)
Cu(1)–N(11)	2.018 (4)	Fe(1)–N(4)	1.970 (4)
Cu(1)–N(12)	2.019 (4)	Fe(1)–N(6)	1.970 (4)
Cu(1)–N(14)	2.032 (4)	Fe(2)–C(16)	1.898 (6)
Cu(1)–N(15)#1	2.355 (5)	Fe(2)–C(17)	1.914 (6)
Cu(1)–N(9)#1	2.481 (5)	Fe(2)–C(18)	1.917 (6)
Fe(1)–C(15)	1.912 (5)	Fe(2)–N(18)	1.959 (4)
Fe(1)–C(13)	1.917 (5)	Fe(2)–N(20)	1.971 (5)
Fe(1)–C(14)	1.919 (6)	Fe(2)–N(22)	1.973 (4)
N(13)–Cu(1)–N(11)	91.22 (16)	C(15)–Fe(1)–N(6)	91.92 (18)
N(13)–Cu(1)–N(12)	178.95 (16)	C(13)–Fe(1)–N(6)	176.77 (18)
N(11)–Cu(1)–N(12)	87.76 (16)	C(14)–Fe(1)–N(6)	92.93 (19)
N(13)–Cu(1)–N(14)	91.68 (16)	N(2)–Fe(1)–N(6)	89.51 (17)
N(11)–Cu(1)–N(14)	173.05 (17)	N(4)–Fe(1)–N(6)	87.32 (16)
N(12)–Cu(1)–N(14)	89.36 (16)	C(16)–Fe(2)–C(17)	88.0 (2)
N(13)–Cu(1)–N(15)#1	89.14 (17)	C(16)–Fe(2)–C(18)	91.2 (2)
N(11)–Cu(1)–N(15)#1	95.00 (16)	C(17)–Fe(2)–C(18)	88.7 (2)
N(12)–Cu(1)–N(15)#1	90.74 (17)	C(16)–Fe(2)–N(18)	176.7 (2)
N(14)–Cu(1)–N(15)#1	91.36 (17)	C(17)–Fe(2)–N(18)	91.8 (2)
C(15)–Fe(1)–C(13)	85.3 (2)	C(18)–Fe(2)–N(18)	92.1 (2)
C(15)–Fe(1)–C(14)	90.5 (2)	C(16)–Fe(2)–N(20)	92.5 (2)
C(13)–Fe(1)–C(14)	88.8 (2)	C(17)–Fe(2)–N(20)	178.95 (19)
C(15)–Fe(1)–N(2)	178.25 (18)	C(18)–Fe(2)–N(20)	90.4 (2)
C(13)–Fe(1)–N(2)	93.22 (19)	C(16)–Fe(2)–N(22)	88.2 (2)
C(14)–Fe(1)–N(2)	90.45 (19)	C(17)–Fe(2)–N(22)	92.52 (19)
C(15)–Fe(1)–N(4)	90.58 (18)	C(18)–Fe(2)–N(22)	178.7 (2)
C(13)–Fe(1)–N(4)	91.02 (18)	N(18)–Fe(2)–N(20)	88.50 (18)
C(14)–Fe(1)–N(4)	178.9 (2)	N(20)–Fe(2)–N(22)	88.41 (18)
N(2)–Fe(1)–N(4)	88.46 (16)		

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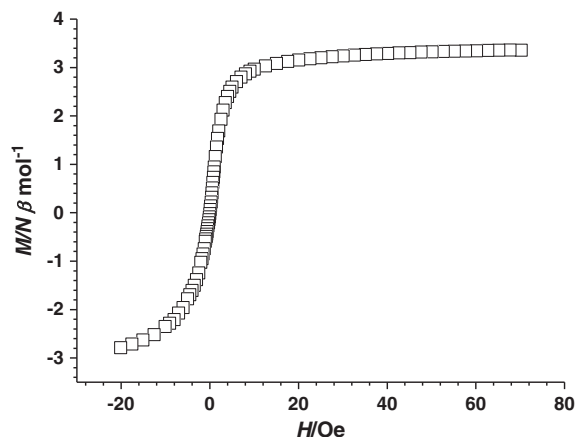

Fig. 3. The isothermal magnetization of compound **1** at 1.8 K.
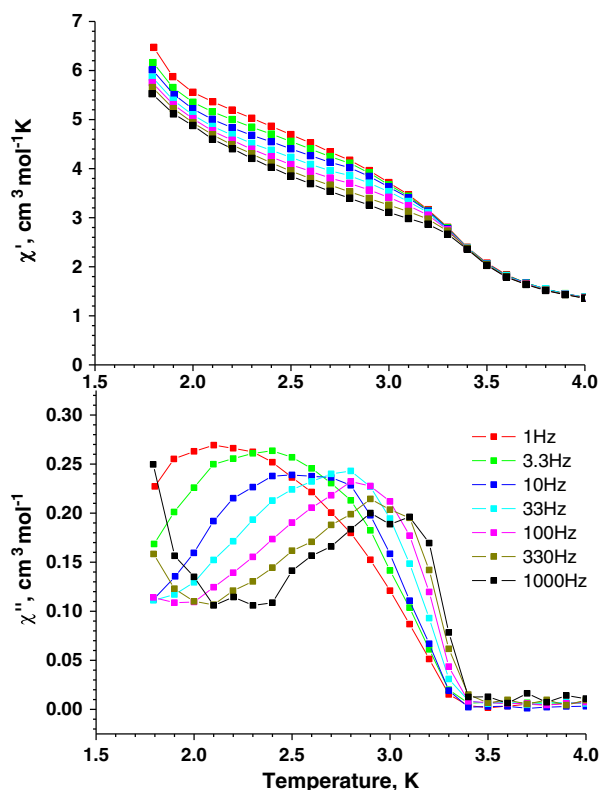
Fig. 4. Frequency dependence of ac magnetic signals of compound **1** at $H_{ac} = 3.5$ Oe and $H_{dc} = 0$ Oe.

peak temperature (T_P) of χ'' is measured by a parameter $\Phi = (\Delta T_P/T_P)/\Delta(\log f) = 0.17$, which is close to a normal value for a superparamagnet [23]. The frequency dependence of T_P of χ'' can be fitted well to the Arrhenius law $\tau = \tau_0 \exp(\Delta/k_B T)$ with the best set of parameters $\tau_0 = 1.59 \times 10^{-8}$ s and $\Delta/k_B = 35.5$ K (Fig. 5), suggesting single chain magnet behavior.

In conclusion, we have synthesized one novel one-dimensional (1D) heterobimetallic cyano-bridged chain complex of squares, [Fe(pzTp)(CN)$_3$]$_2$Cu(4-styrylpyridine)$_2$·2H$_2$O·4CH$_3$OH (**1**), by using of the tailored cyanometalate precursor, Bu$_4$N[Fe(pzTp)(CN)$_3$] as the building block and 4-styrylpyridine as monodentate ligand to react with fully solvated Cu^{II} cations. Magnetic measurements indicate that compound **1** exhibits intrachain ferromagnetic coupling and single-chain magnets behavior.
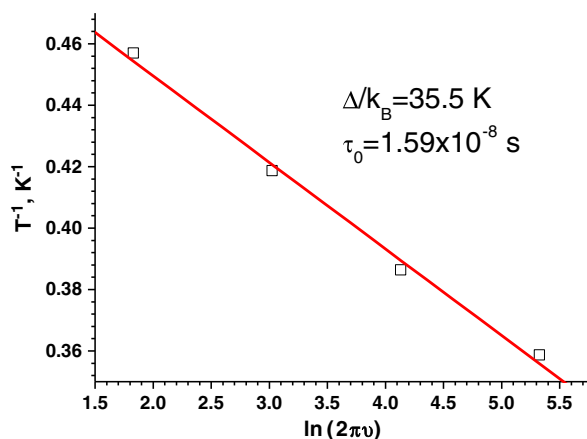

Fig. 5. The fit of the $\tau(T)$ data to the Arrhenius law.

Appendix A. Supplementary material

CCDC 865717 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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[16] The title compound [Fe(pzTp)(CN)$_3$]$_2$Cu(4-styrylpyridine)$_2$·2H$_2$O·4CH$_3$OH was synthesized by a diffusion method in a test tube. A mixture of methanol and water (1:1, 2 mL) was gently layered on the top of a solution of Cu(ClO$_4$)$_2$.6H$_2$O (18.53 mg, 0.05 mmol) in water (3 mL). A solution of [Bu$_4$N][Fe(pzTp)(CN)$_3$] (66.0 mg, 0.1 mmol) and 4-styrylpyridine (18.0 mg, 0.1 mmol) in methanol (10 mL) was added carefully as the third layer. Red crystals were obtained after 3 weeks, washed with ethanol and ether, and dried in air. Yield: 49%. Element analysis, calculated for C$_{60}$H$_{66}$B$_2$CuFe$_2$N$_{24}$O$_6$: C 50.84, H 4.66, N 23.72; Found: C 50.88, H 4.59, N 23.66. IR (solid KBr pellet ν/cm^{-1}): 3442 br, 3145 w, 2166 m, 1613 s, 1501 m, 1408 s, 1388 m, 1305 s, 1212 m, 1107 m, 1066 s, 1029 w, 873 w, 858 m, 809 m, 792 m, 762 s, 728 w, 691 w, 615 w, 544 w, 496 w.
[17] Crystal structure analysis: The data were collected at a temperature of 293 ± 2 K on a Bruker Smart APEX II X-diffractometer equipped with graphite monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å) using the SMART and SAINT programs. Indexing and unit cell refinement were based on all observed reflections from those 72 frames. The structure was solved in the space group P−1 by direct method and refined by the full-matrix least-squares fitting on F2 using SHELXTL–97 [24]. All non–hydrogen atoms were treated anisotropically. Hydrogen atoms of organic ligands were generated geometrically, fixed isotropic thermal parameters, and included in the structure factor calculations. Crystal data for 1: C$_{60}$H$_{66}$B$_2$CuFe$_2$N$_{24}$O$_6$, M = 1416.23, Triclinic, P−1, a = 14.380(5) Å, b = 14.434(4) Å, c = 16.450(5) Å, α = 75.910(18)°, β = 85.60(2)°, γ = 87.95(2)°, V = 3301.6(16) Å^3, Z = 2, Dc = 1.425 g·cm^{-3}, μ = 0.822 mm^{-1}. Data were collected on a single crystal with dimensions 0.22×0.13×0.11 mm^3. 23046 reflections were measured with ω-scans, in the range of 1.98° ≤ θ ≤ 25.0° (−17 ≤ h ≤ 16, −17 ≤ k ≤ 17, −19 ≤ l ≤ 19), 11305 independent reflections (Rint = 0.073). Final R1 = 0.0617, wR2 = 0.1141 [I > 2σ (I)], and the goodness–of–fit on F^2 is 0.959.
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