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氰根桥联 $Fe^{Ⅲ}$-$Cu^{Ⅱ}$一维配合物{[Fe(1-CH_3im)$(CN)_4$(μ-CN)Cu(cyclam)]·H_2O}$_n$的合成、结构及磁性研究

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摘要：基于构筑单元 K_2[Fe(1-CH_3im)$(CN)_5$]和[Cu(cyclam)]$(ClO_4)_2$,合成了一个氰根桥联 $Fe^{Ⅲ}$-$Cu^{Ⅱ}$中性一维化合物{[Fe(1-CH_3im)$(CN)_4$(μ-CN)Cu(cyclam)]·H_2O}$_n$ (1-CH_3im=1-甲基咪唑;cyclam=1,4,8,11-四氮杂环十四烷) (**1**),并通过 X-射线单晶分析表征其结构特征。结果表明:化合物(**1**)是由氰根桥联的杂金属组成的聚合物,其结构属于三斜晶系,$P\bar{1}$ 空间群,a=0.832 56(17) nm,b=0.899 38(18) nm,c=0.998 3(2) nm,α=111.94(3)°,β=95.06(3)°,γ=116.90(3)°,V=0.587 7(2) nm^3,Z=1,D_c=1.554 g·cm^{-3},μ=1.558 mm^{-1},F(000)=286,R_1=0.051 9,wR_2=0.135 3。磁性研究表明:配合物 **1** 中 $Cu^{Ⅱ}$和低自旋的 $Fe^{Ⅲ}$离子之间存在弱的铁磁耦合作用。

关键词：氰根桥联；晶体结构；磁性；杂金属
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Synthesis, Crystal Structure and Magnetic Properties of a One-Dimensional Cyanide-Bridged $Fe^{Ⅲ}$-$Cu^{Ⅱ}$ Complex {[Fe(1-CH_3im)$(CN)_4$(μ-CN)Cu(cyclam)]·H_2O}$_n$

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Abstract: A new one-dimensional cyanide-bridged $Fe^{Ⅲ}$-$Cu^{Ⅱ}$ complex {[Fe(1-CH_3im)$(CN)_4$(μ-CN)Cu(cyclam)]·H_2O}$_n$ (1-CH_3im=1-methylimidazole, cyclam=1,4,8,11-tetraazacyclotetradecane) (**1**) has been synthesized by the reaction of [Cu(cyclam)]$(ClO_4)_2$ and a pentacyanideferrite building blocks K_2[Fe(1-CH_3im)$(CN)_5$]. Single crystal X-ray diffraction analysis reveals the structure of complex **1** is polymer type with two different metal centers which is alternated linked by cyanide group from the [Fe(1-CH_3im)$(CN)_5]^{2-}$ building blocks. Complex **1** ($C_{19}H_{32}CuFeN_{11}O$, M_r=549.95) crystallizes in triclinic space group $P\bar{1}$ with a=0.832 56(17) nm, b=0.899 38(18) nm, c=0.998 3(2) nm, α=111.94(3)°, β=95.06(3)°, γ=116.90(3)°, V=0.587 7(2) nm^3, Z=1, D_c=1.554 g·cm^{-3}, μ=1.558 mm^{-1}, F(000)=286, the final R_1=0.051 9 and wR_2=0.135 3. Magnetic investigations show that complex **1** exhibits a weak ferromagnetic coupling between $Cu^{Ⅱ}$ and low-spin $Fe^{Ⅲ}$ through the cyanide bridge. CCDC: 908099.

Key words: cyanide-bridged; crystal structure; magnetic property; heterometalllic

0 Introduction

In the past several decades, many metal complexes which show interesting and molecular topology structure and properties have been obtained by rational molecular design[1-9]. As one of the most known bridging groups, cyanide group has manifested unique roles for the design and assembly of

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heterometallic even heterotrimetallic molecular magnetic systems because the topological structures and the nature of the magnetic interactions between different metal ions can be relatively easily controlled and anticipated. Therefore, cyanide-bridged complexes have been paid much attention[10-15].

The design and synthesis of suitable and stable cyanide-containing building blocks is always a challenging task for the preparation of novel cyanide-bridged molecular magnetic materials. In this process, the control and selection of the number and position of cyanide group and the charge number of cyanide-containing building blocks are significantly basic factors for the cyanide-bridged complexes with special topological structures and magnetic properties. Up to now, the stable and suitable cyanide-containing building blocks reported are still very limited. Our group devoted great efforts to the exploitation of cyanide-containing building blocks and the assembly of cyanide-bridged complexes in the past ten years[16-18]. Recently, we use pentacyanide-containing precursor K_2[Fe(1-CH_3im)$(CN)_5$] to synthesize a cyanide-bridged one-dimensional neutral chain-like $Fe^{Ⅲ}$-$Cu^{Ⅱ}$ complex {[Fe(1-CH_3im)$(CN)_4$(μ-CN)Cu(cyclam)]·H_2O}$_n$ (**1**). Herein, we report its synthesis, crystal structure and magnetic properties.

1 Experimental

1.1 Materials and physical measurements

Elemental analyses of carbon, hydrogen and nitrogen were performed on a German Elementary Vario EL Ⅲ. The infrared spectroscopy on KBr pellets was carried out with a Magna-IR 750 spectrophotometer in the 4 000 ~400 cm^{-1} region. Magnetic properties were measured on a Quantum Design MPMS SQUID magnetometer using crystal sample. The experimental susceptibilities were corrected for diamagnetism estimated according to Pascal′s constants.

Chemicals were purchased from commercial sources and used without further handling. The precursor K_2[Fe(1-CH_3im)$(CN)_5$] and [Cu(cyclam)]$(ClO_4)_2$ were reported in the literatures[19-20].

1.2 Synthesis of {[Fe(1-CH_3im)$(CN)_4$(μ-CN)Cu(cyclam)]·H_2O}$_n$ (1)

Brown block single crystal of {[Fe(1-CH_3im)$(CN)_4$(μ-CN)Cu(cyclam)]·H_2O}$_n$ was prepared at room temperature by carefully layering of a solution of [Cu(cyclam)]$(ClO_4)_2$ (0.1 mmol) in methanol/water (4∶1, *V*/*V*, 10 mL) and a solution of K_2[Fe(1-CH_3im)$(CN)_5$] (0.1 mmol) ethanol (10 mL). After about 2 days, the products were collected by filtration. Yield: 28.16 mg (51.2%). Anal. Calcd(%) for $C_{19}H_{32}CuFeN_{11}O$: C, 41.49; H: 5.86; N: 28.02. Found(%): C: 41.35; H: 5.90; N: 27.99. Selected IR frequencies (KBr disk, cm^{-1}): 2 110, 2 150(m, $\nu_{C\equiv N}$).

1.3 X-ray structure determination

The crystal data is listed in Table 1. The structure were solved by direct methods with the SHELXS-97 program[21] and refined by full-matrix least-squares on F^2 with the SHELXL-97 program[22]. All non-hydrogen atoms were refined by anisotropic thermal parameters and the hydrogen atoms by isotropic parameters. Hydrogen atoms bound to carbon atoms were added by the HFIX commands in SHELXL-97 program geometrically. The Flack parameter was based on 2 421 Friedel pairs, and the Flack parameter value (0.01(2)) for the assigned absolute configuration suggests that it is correct to a high accuracy. All Figures were created by the DIAMOND program.

CCDC: 908099.

2 Results and discussion

2.1 Crystal structure description

Single-crystal X-ray diffraction shows the crystal structure of complex **1** is a cyanide-bridged one-dimensional neutral chain. The chain is composed of cyanide-bridged alternating [Fe(1-CH_3im)$(CN)_5$]$^{2-}$ and [Cu(cyclam)]$^{2+}$ fragments (Fig.1). In the chain, two [Cu(cyclam)]$^{2+}$ units are linked by two cyanide groups from [Fe(1-CH_3im)$(CN)_5$]$^{2-}$ building blocks. The labeling scheme for the chain-like structure of complex **1** is shown in Fig.2, and selected bond distances and angles are listed in Table 2.

The Fe atom center is hexacoordinated with one

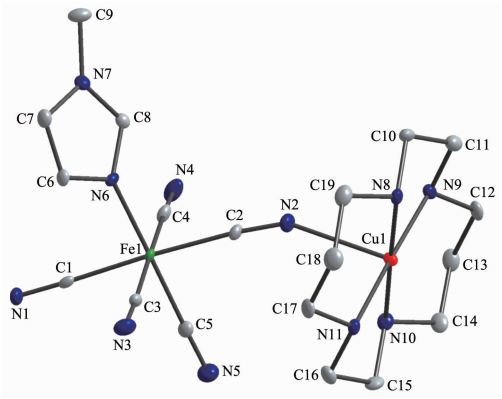
Table 1 Crystal data and experimental details for complex 1

Empirical formula	$C_{19}H_{32}CuFeN_{11}O$	Absorption Coefficient / mm^{-1}	1.558
Formula weight	549.95	Max. and Min. Transmission	0.818, 0.754
Wavelength / nm	0.071 073	D_c / ($g\cdot cm^{-3}$)	1.554
Crystal system	Triclinic	$F(000)$	286
Space group	$P\bar{1}$	θ range for data collection / (°)	4.16~27.48
a / nm	0.832 56(17)	Reflections collected / unique	8 349 / 5 040
b / nm	0.899 38(18)	R_{int}	0.051 9
c / nm	0.998 3(2)	Data / restraints / params	5 040 / 3 / 299
α / (°)	111.94(3)	Reflections with $I>2\sigma(I)$	4 532
β / (°)	95.06(3)	Goodness-of-fit on F^2	1.028
γ / (°)	116.90(3)	R_1 ($I>2\sigma(I)$)	0.048 7
V / nm^3	0.587 7(2)	wR_2 (all data)	0.138 4
Z	1	Flack parameter	0.01(2)

Table 2 Selected bond distances (nm) and bond angles (°)

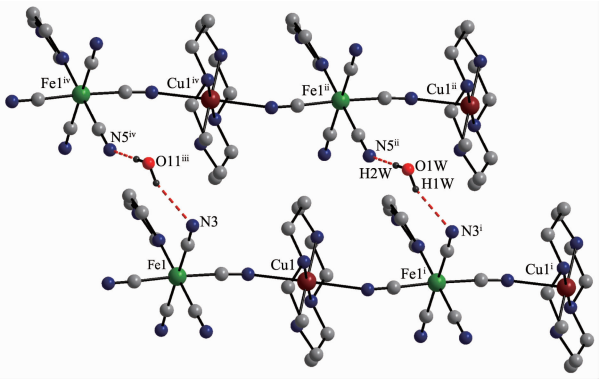
Fe1-C1	0.194 9(5)	Fe1-C2	0.196 0(5)	Cu1-N9	0.204 0(4)
Fe1-C3	0.195 4(5)	Fe1-C4	0.196 3(5)	Cu1-N10	0.203 0(4)
Fe1-C5	0.192 0(5)	Fe1-N6	0.197 9(4)	Cu1-N11	0.201 8(4)
Cu1-N2	0.241 9(4)	Cu1-N8	0.203 2(4)	Cu1-Fe1	0.531 4(8)
Cu1-N1	0.252 1(5)				
Cu1-N2-C2	150.8(3)	Cu1-N1-C1	144.2(3)	Fe1-C5-N5	178.8(4)
C1-Fe1-C2	176.5(2)	Fe1-C1-N1	177.7(4)	Fe1-C4-N4	178.2(4)
Fe1-C3-N3	177.5(4)	Fe1-C2-N2	174.9(4)		

nitrogen atom from 1-CH_3im ligand and five nitrogen atoms belonging to cyanide groups, which forms a slightly distorted octahedral geometry. Two of the five cyanide groups link the $[Cu(cyclam)]^{2+}$ cations in an end-to-end mode to generate an infinite chain with the other three equatorial cyanide groups intact. The average bond distance of Fe-C is 0.194 8 nm, and the bond distance of Fe1-N6 (1-CH_3im ligand) is 0.197 9(4) nm. The angles of Fe-C-N including both bridging and non-bridging cyanide in complex **1** are almost linear with the values ranging from 174.9(4)° (Fe1-C2-N2) to 178.8(4)° (Fe1-C5-N5). Besides, the C1-Fe1-C2 angle (176.5(2)°) is also nearly linear.



Lattice water and hydrogen atoms have been omitted for clarity

Fig.1 Crystal structure of asymmetric unit in complex **1** with thermal ellipsoids at 30% probability level



Iirrelevant H atoms have been omitted for clarity; Symmetry operations: [i] x, $-1+y$, $-1+z$; [ii] $-1+x$, $-1+y$, $-1+z$; [iii] x, $1+y$, $1+z$; [iv] $-1+x$, y, z

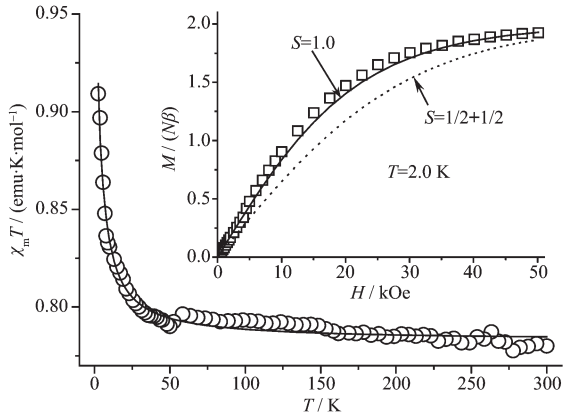
Fig.2 One-dimensional structure and hydrogen bonds in complex **1**

Copper(Ⅱ) center displays a regular octahedron composed of the four nitrogen atoms of cyclam ligand in the equatorial plane and the two nitrogen atoms from cyanide groups belonging to $[Fe(1\text{-}CH_3im)(CN)_5]^{2-}$ in the *trans* positions. The in-plane Cu-N bond lengths span from 0.201 8(4) nm (Cu1-N11) to 0.204 0(4) nm (Cu1-N9), while the apical Cu-N bond distances are obviously longer with the Cu-N distances of 0.241 9(4) nm (Cu1-N2) and 0.252 1(5) nm (Cu1-N1), leading to the elongated tetragonal bipyramide symmetry of a $[CuN_6]$ unit. The two slightly bent Cu–N≡C angles are obviously different with the value of 150.8 (3)° for Cu1-N2-C2 and 144.2(3)° for Cu1-N1-C1.

The cell packing diagram (Fig.2) of complex **1** shows the existence of interchain hydrogen bonds between the water molecules and the nitrogen atoms of cyanide groups, and these hydrogen bonds link the one-dimensional chains into the two-dimensional layer structure.

2.2 Magnetic property of complex 1

The magnetic susceptibilities have been measured in the temperature ranging from 2 to 300 K under an applied field of 2 kOe, which is plotted as χ_mT-T presented in Fig.3. At 300 K, the χ_mT value of complex **1** is 0.78 emu·K·mol^{-1}, which is almost equal to the spin-only value of 0.75 emu·K·mol^{-1} anticipated for two independent S=1/2 of Cu^{Ⅱ} and low-spin Fe^{Ⅲ}. As the temperature is decreased, the χ_mT value increase slowly until about 50 K, and then they increase quickly to 0.899 emu·K·mol^{-1} at 2.4 K. The χ_mT curve shows that the magnetic interaction between Cu^{Ⅱ} and low-spin Fe^{Ⅲ} through cyanide group is weak ferromagnetic. In the whole temperature range, $1/\chi_m$-T curve obeys the Curie-Weiss expression with the Weiss constant θ=1.03 K and Curie constant C=0.78 K·mol^{-1} for complex **1**. The positive Weiss constant also displays the presence of weak ferromagnetic coupling between Cu^{Ⅱ} and low-spin Fe^{Ⅲ}.



Inset: Field dependence of magnetization, the line and the broken line represent the Brillouin function that correspond to S=1 and non-interacting S=1/2+1/2 based on g=2.0, respectively

Fig.3 Temperature dependence of χ_mT for complex **1** measured under an applied field of 2 kOe

The field (H) dependence of the magnetization (M) for complex **1** was collected at 2 K in the field range of 0~50 kOe (inset of Fig.3). The field dependence of the magnetization of complex **1** is almost in agreement with their corresponding Brillouin curve for the S=1 spin state with g=2.00. However, The magnetization data are higher than the Brillouin curve deduced for an isolated Fe(Ⅲ) spin (S=1/2) and Cu(Ⅱ) spin (S=1/2) with g=2.00, further demonstrating that the slight ferromagnetic coupling exist in complex **1**.

In order to do a quantitative fitting of the magnetic data, we treated the magnetic data by taking a one-dimensional uniformly spaced chain model of classical spins derived by Fisher[23] according to the following expressions:

$$\chi_{chain}=\frac{Ng^2\beta^2}{3kT}\frac{1+u}{1-u}\times S_d(S_d+1) \quad (1)$$

$$\chi_m=\chi_{chain} \quad (2)$$

Where $u=\coth\frac{JS_d(S_d+1)}{kT}-\frac{kT}{JS_d(S_d+1)}$

The best-fit parameters are g=2.092 1 and J=0.349 7 cm^{-1}. In fact, the one-dimensional complex is non-uniform, which can be treated as alternating uniform Fe^{Ⅲ}-Cu^{Ⅱ} dimers[24] with different intradimeric and intrachain (also interdimer) exchange constants (J_d vs J_c, see Fig.4).

$$\chi_d=\frac{2Ng^2\beta^2}{3kT}\left[\frac{1}{3+e^{-2J_d/(kT)}}\right] \quad (1)$$

$$\chi_d=\frac{Ng^2\beta^2}{3kT}S_d(S_d+1) \quad (2)$$

$$\chi_{chain}=\frac{Ng^2\beta^2}{3kT}\frac{1+u}{1-u}\times S_d(S_d+1) \quad (3)$$

$$\chi_m=\chi_{chain} \quad (4)$$

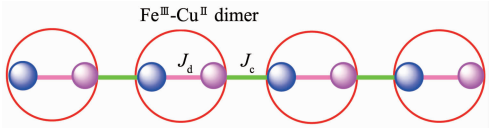


Fig.4 One-dimensional magnetic model for complex **1**

Where $u=\coth\frac{J_cS_d(S_d+1)}{kT}-\frac{kT}{J_cS_d(S_d+1)}$

On the basis of this model, the best fits parameters are J_c=0.12 cm^{-1}, J_d=0.459 7 cm^{-1}, and g=2.092 1. The small magnetic coupling constants based on the two models show that the magnetic coupling between Fe^{III} and Cu^{II} ions in complex **1** is weak ferromagnetic coupling, which is reasonable and can comparable to those of most cyanide-bridged Cu^{II} and low-spin Fe^{III} complexes[25-30].

3 Conclusions

In summary, a novel neutral cyanide-bridged Fe^{III}-Cu^{II} complex has been obtained based on K_2[Fe(1-CH_3im)$(CN)_5$] and [Cu(cyclam)]$(ClO_4)_2$, which shows one-dimensional structure. Magnetic investigations show that the complex exhibits a weak ferromagnetic coupling between Cu^{II} and low-spin Fe^{III}, and the theoretical models presented fit the experimental data quantitatively.

References:

[1] Ma Y S, Li Y Z, Zheng L M, et al. *Inorg. Chem.*, **2008**,**47**:4536-4544

[2] Li B, Chen L Q, Wei R J, et al. *Inorg. Chem.*, **2011**,**50**:424-426

[3] You Y S, Yoon J H, Lim J H, et al. *Inorg. Chim. Acta*, **2007**,**360**:2523-2531

[4] YAO Jing (姚景), XING Yan-Yan (邢燕燕), XU Yan-Yan (徐艳燕), et al. *Chinese J. Inorg. Chem.* (*Wuji Huaxue Xuebao*), **2008**,**24**:1636-1642

[5] Colacio E, Dominguez-Vera J M, Ghazi M, et al. *Chem. Commun.*, **1998**:1071-1072

[6] Shen Z, Zuo J L, Gao S, et al. *Angew. Chem. Int. Ed.*, **2000**, **39**:3633-3635

[7] Cha M J, Shin J W, Lee Y H, et al. *Inorg. Chem. Commun.*, **2009**,**12**:520-522

[8] Dong D P, Liu T, Zheng H, et al. *Inorg. Chem. Commun.*, **2012**,**24**:153-156

[9] NI Zhong-Hai(倪中海), NIE Jing(聂景), LI Guo-Ling(李国玲), et al. *Chinese J. Inorg. Chem.*(*Wuji Huaxue Xuebao*), **2012**,**2**:411-416

[10]Wang S, Ding X H, Li Y H, et al. *Coord. Chem. Res.*, **2012**, **256**:439-464

[11]Yao M X, Zheng Q, Gao F, et al. *Sci. China Chem.*, **2012**, **55**:1022-1030

[12]Palii A, Tsukerblat B, Klokishner S, et al. *Chem. Soc. Rev.*, **2011**,**40**:3130-3156

[13]Trávnček Z, Herchel R, Mikulík J, et al. *J. Solid State Chem.*, **2010**,**183**:1046-1054

[14]Beltran L M C, Long J R. *Acc. Chem. Res.*, **2005**,**38**:325-334

[15]Kou H Z, Liao D Z, Cheng P, el al. *J. Chem. Soc., Dalton Trans.*, **1997**:1503-1506

[16]Ni Z H, Kou H Z, Zhao Y H, et al. *Inorg. Chem.*, **2005**,**44**:2050-2059

[17]Ge C H, Kou H Z, Ni Z H, et al. *Chem. Lett.*, **2005**,**34**:1280-1281

[18]Li G L, Nie J, Chen H, et al. *Inorg. Chem. Commun.*, **2012**, **19**:66-69

[19]Kamaluddin, Mala N, Sushama W D. *Bull. Chem. Soc. Jpn.*, **1989**,**62**:3291-3297

[20]Kolinski R A, Korybut-Daszkiewicz B. *Inorg. Chim. Acta*, **1975**,**14**:237-245

[21]Sheldrick G M. *Acta Crystallogr.*, **2008**,**A64**:112-122

[22]Sheldrick G M. *SHELXL*-97, *Program for Refinement of Crystal Structure*, University of Gottingen, Germany, **1997**.

[23]Fischer M E. *Am. J. Phys.*, **1964**,**32**:343-346

[24]Nie J, Li G L, Miao B X, et al. *Chinese J. Struct. Chem.*, **2012**,**31**:1129-1134

[25]Bieńko A, Suracka K, Mroziński J, et al. *Polyhedron*, **2010**, **29**:2546-2552

[26]Colacio E, Domínguez-Vera J M, Ghazi M, et al. *J. Chem. Soc., Dalton Trans.*, **2000**:505-509

[27]Zhang B, Ni Z H, Cui A L, et al. *New J. Chem.*, **2006**,**30**:1327-1332

[28]Parker R J, Lu K D, Batten S R, et al. *J. Chem. Soc., Dalton Trans.*, **2002**:3723-3730

[29]Kou H Z, Zhou B C, Wang R J, et al. *Inorg. Chem.*, **2003**, **42**:7658-7665

[30]Lu T B, Shi H X, Chen S, el at. *J. Inorg. Organomet. Polym.*, **1999**,**9**:165-178