氰根桥联 Cr^{III}-Cu^{II}一维配合物{[Cu(cyclam)][Cr(bpb)(CN)₂]₂·2H₂O}ₙ 的合成、结构与磁性

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摘要：基于构筑单元 K[Cr(bpb)(CN)₂]和[Cu(cyclam)](ClO₄)合成了一个氰根桥联的 Cr^{III}-Cu^{II}一维化合物{[Cu(cyclam)][Cr(bpb)(CN)₂]₂·2H₂O}ₙ,[cyclam=1,4,8,11-四氮杂环十四烷;bpb²⁻=1,2-二(2-吡啶甲酰胺基)苯](**1**),并通过 X-衍射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 2 种不同金属组成的聚合物,其结构属于三斜晶系,$P\bar{1}$ 空间群,a=0.9667 3(19) nm,b=1.345 1(3) nm,c=1.382 0(3) nm,α=77.12(3)°,β=76.93(3)°,γ=82.02(3)°,V=1.699 1(6) nm³,Z=2,D_c=1.567 g·cm⁻³,μ=1.086 mm⁻¹,$F(000)$=828,R_1=0.0413,wR_2=0.1200。磁性研究表明：配合物 **1** 中的 Cr^{III}离子和 Cu^{II}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 Cr^{III}-Cu^{II} Complex {[Cu(cyclam)][Cr(bpb)(CN)₂]₂·2H₂O}ₙ

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Abstract: A one-dimensional cyanide-bridged Cr^{III}-Cu^{II} complex {[Cu(cyclam)][Cr(bpb)(CN)₂]₂·2H₂O}ₙ (cyclam=1, 4,8, 11-tetraazacyclotetradecane, bpb²⁻=1,2-bis (pyridine-2-carboxamido)-benzenate) (**1**) has been synthesized by the reaction of building blocks [Cu(cyclam)](ClO₄)₂ and K[Cr(bpb)(CN)₂]. Single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in triclinic space group $P\bar{1}$ with a=0.966 73 (19) nm, b=1.345 1 (3) nm, c=1.382 0(3) nm, α=77.12(3)°, β=76.93(3)°, γ=82.02(3)°, V=1.699 1(6) nm³, Z=2, D_c=1.567 g·cm⁻³, μ=1.086 mm⁻¹, $F(000)$=828, R_1=0.041 3, wR_2=0.120 0, the structure of complex **1** is a type of polymer with two different metal centers which are alternatively linked by cyanide group. Magnetic investigations indicate that complex **1** exhibits a weak ferromagnetic coupling between Cr^{III} and Cu^{II} centers through the cyanide bridge. CCDC: 972349.

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

0   Introduction

In the past decades, heterometallic complexes as one of the most known molecular-based magnetic materials have attracted much attention because of their fascinating structural features and excellent

magnetic properties, thus far, a number of heterometallic complexes molecular-based magnetic materials have been synthesized and characterized structurally and magnetically [1-4]. Among those complexes, cyanide group plays unique roles in design and assembly of heterobimetallic even heterotrimetallic species because of its asymmetric character [5-11]. Cyanide-bridged heterometallic complexes which magnetic exchange interaction occur through cyanide bridge have made great contributions for the building of magneto-structural relationships and the elucidation of the nature of magnetic coupling[12-16].

The number and position of cyanide group and the charge of cyanide-containing building blocks are very significant factors for building cyanide-bridged complexes with fascinating structural and excellent magnetic properties[17-20]. However, the design and synthesis of the stable and suitable cyanide-containing building blocks are still a challenge. Compared with cyanide-bridged heterometallic Fe^{III}-M (M=Cu^{II}, Ni^{II}, Co^{II}, Mn^{II}, Mn^{III} et al.) complexes, Cr^{III}-M are still limited due to the shortage of stable and suitable cyanide-containing building blocks[21-23]. In our group, we have focused our efforts on the design and synthesis of new cyanide-containing building blocks and the assembly of new cyanide-bridged complexes based on them in the past several years[24-26]. Recently, we synthesized a one-dimensional cyanide-bridged Cr^{III}-Cu^{II} complex {[Cu(cyclam)][Cr(bpb)(CN)$_2$]$_2$·2H$_2$O}$_n$ (1) by using building block K[Cr(bpb)(CN)$_2$]. Herein, we report its synthesis, crystal structure and magnetic properties.

1　Experimental

1.1　Materials and physical measurements

Elemental analyses (C, H and N) were carried out on an Elementary Vario EL instrument. The infrared spectra of solid samples on KBr pellets were recorded on a Nicolet 7199B FT/IR spectrophotometer in the region of 4 000~400 cm^{-1}. Magnetic properties measurements on crystal samples were carried out on a Quantum Design MPMS SQUID magnetometer. The experimental susceptibilities were corrected for the diamagnetism estimated based on Pascals tables.

All chemicals and solvents were purchased from commercial sources and used without further handing. The precursors [Cu(cyclam)](ClO$_4$)$_2$[27] and K[Cr(bpb)(CN)$_2$] [28] were prepared according to literature methods.

1.2　Preparation of complex 1

Dark red block single crystals of complex **1** were prepared at room temperature by carefully mixing a purple 50% aqueous methanol solution (10 mL) of [Cu(cyclam)](ClO$_4$)$_2$ (0.1 mmol, 46.3 mg) and a red methanol solution (5 mL) of K[Cr(bpb)(CN)$_2$] (0.1 mmol, 45.9 mg). The single crystals were carefully collected after about three days. Yield: 0.040 g (49.9%). Anal. Calcd.(%) for CuCrC$_{30}$H$_{38}$N$_{10}$O$_7$Cl: C: 44.95; H: 4.78; N: 17.47. Found(%): C: 44.88; H: 4.79; N: 17.38. Selected IR frequencies (KBr disk, cm^{-1}): 2 225(m, $\nu_{C≡N}$), 1 622(s, $\nu_{C=O}$), 1 089(vs, ν_{O-Cl}).

1.3　X-ray data collection and structure refinement

The structure of complex **1** was solved by direct methods with the SHELXS-97 program [29] and refined by full-matrix least-squares methods on F^2 with the SHELXS-97 [30]. The diffraction data were collected at 123 K on a Bruker Smart Apex Ⅱ CCD diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ =0.071 073 nm). Anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using a riding model. Images were created by using DIAMOND program. Crystallographic data and structure refinement parameters are listed in Table 1, and selected bond lengths and angles of complex **1** are listed in Table 2.

CCDC: 972349.

2　Results and discussion

2.1　Crystal structure of complex 1

Single crystal X-ray diffraction analysis reveals that the structure of complex **1** is a one-dimensional cationic polymer [Cu(cyclam)][Cr(bpb)(CN)$_2$]$^+$ with free ClO$_4$ $^-$ as counteranions. The wavelike chain is

Table 1　Crystal data and structure refinement parameters for complex 1

Empirical formula	$CuCrC_{30}H_{38}N_{10}O_7Cl$	Absorption Coefficient / mm^{-1}	1.086
Formula weight	801.69	Max. and Min. Transmission	0.939, 0.900
Crystal system	Triclinic	D_c / (g·cm^{-3})	1.567
Space group	$P\bar{1}$	$F(000)$	828
a / nm	0.966 7(19)	θ range for data collection / (°)	3.09~26.00
b / nm	1.345 1(3)	Reflections collected / unique	17 933/6 608
c / nm	1.382 0(3)	R_{int}	0.051 6
α / (°)	77.12(3)	Data / restraints / params	6 608/0/451
β / (°)	76.93(3)	Reflections with $I>2\sigma(I)$	6 138
γ / (°)	82.02(3)	Goodness-of-fit on F^2	0.994
V / nm^3	1.699 1(6)	R_1 $(I>2\sigma(I))$	0.041 3
Z	2	wR_2 (all data)	0.120 0
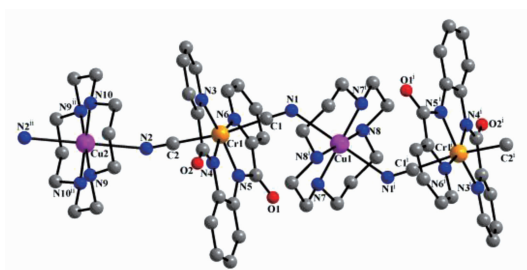
Symmetry codes: ^{i}1−x, 1−y, 1−z, ^{ii}2-x, −y, −z

Fig.1　One-dimensional crystal structure of complex **1**

comprised of $[Cr(bpb)(CN)_2]^-$ units and $[Cu(cyclam)]^{2+}$ fragments which are alternatively linked by cyanide group. In the one-dimensional chain, each [Cu (cyclam)]$^{2+}$ group is linked to two $[Cr(bpb)(CN)_2]^-$ ions in the trans positions. The labeling scheme of the chain-like structure of complex **1** is shown in Fig.1.

The Cr^{III} center is hexacoordinated with two bridging cyanide nitrogen atoms and four coplanar nitrogen atoms of bpb^{2-} ligand, which forms a slightly distorted octahedron. The average bond distances of Cr-N(amide) and Cr-N(pyridine) are 0.197 11(19) and 0.208 95(18) nm, respectively. Apparently, the average bond lengths of Cr-N (amide) are shorter than Cr-N (pyridine) in complex **1**, which is in agreement with the fact that the deprotonated amide group is a very strong σ-donor. The average bond distance of Cr-C is 0.209 9(2) nm. The angles of Cr1-C1-N1 and Cr1-C2-N2 are almost linear with the value of 176.86(19)° and 176.99(18)°, respectively. Besides, the C1-Cr1-C2 bond angle with the value of 171.99(8)° is also nearly

linear.

There are two independent Cu^{II} centers in the one-dimensional chain of complex **1**, each Cu^{II} center is also hexacoordinated with six nitrogen atoms which come from two bridging cyanides in the axial position and cyclam ligand in the equatorial plane, forming an elongated octahedron. The in-plane Cu-N bond lengths span from 0.200 49(17) to 0.204 86(18) nm, while the apical Cu-N bond lengths are relatively long (0.248 94(18) nm for Cu1-N1 and 0.255 28(18) nm for Cu2-N2) due to Jahn-Teller effect of Cu^{II} ion. The angles of the in-plane N-Cu-N range from 85.70(8)° to 94.30(8)°, and the angles of Cu1-N1-C1 and Cu2-N2-C2 are 130.87(8)° and 146.93(8)°, respectively. The distances of the intramolecular Cu^{II} and Cr^{III} centers separated through bridging cyanide are 0.521 03(17) nm for Cr1⋯Cu1 and 0.554 15(18) nm for Cr1⋯Cu2.

The cell packing diagram (Fig.2) of complex **1** shows the existence of interchain hydrogen bonds between the oxygen atoms from the free water
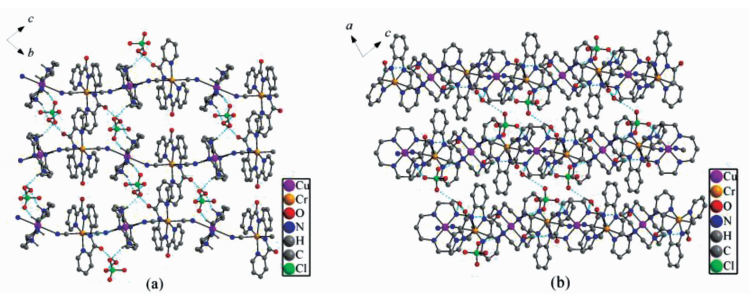
Fig.2　Supermolecular structure for complex **1**, formed by hydrogen-bond interactions: (a) along the a axis; (b) along the b axis

Table 2　Selected bond distances (nm) and bond angles (°) of complex 1

Cr1-C1	0.210 2(2)	Cr1-C2	0.209 6(2)	Cu1-N1	0.248 9(1)
Cr1-N3	0.209 45(18)	Cr1-N4	0.197 30(19)	Cu1-N8	0.200 49(19)
Cr1-N5	0.196 93(19)	Cr1-N6	0.208 45(19)	Cu1-N7	0.204 86(19)
Cu2-N2	0.255 28(22)	Cu2-N9	0.202 07(19)	Cu2–N10	0.201 74(19)
Cr1···Cu1	0.521 03(17)	Cr1···Cu2	0.554 15(18)	Cr1-C1-N1	176.86(19)
Cr1-C2-N2	176.99(18)	C1-Cr1-C2	171.99(8)	N3-Cr1-N4	79.53(7)
N4-Cr1-N5	81.16(8)	N5-Cr1-N6	79.32(8)	N6-Cr1-N3	119.99(8)
Cu1-N1-C1	130.87(8)	N8-Cu1-N7	94.30(8)	N8-Cu1-N7^i	85.70(8)
N9-Cu2-N10	93.76(8)	N9-Cu2-N10^{ii}	86.24(8)	Cu2-N2-C2	146.93(8)

molecules, bpb^{2-} ligands and ClO$_4^-$ anions and the nitrogen atoms from cyclam ligands, and these hydrogen bonds link the chains into the three-dimensional supermolecular structure.

2.2　Magnetic property of complex 1

The magnetic susceptibilities of complex **1** were measured in the 2~300 K temperature range under an applied field of 2 000 Oe, which is plotted as $\chi_m T$-T and χ_m^{-1}-T in Fig.3, where χ_m is the magnetic susceptibility per Cu^{III}Cr^{II} unit. At 300 K, the value of $\chi_m T$ for complex **1** is 2.27 emu·K·mol^{-1}, which is almost equal to the anticipated spin-only value (2.25 emu·K·mol^{-1}) of the isolate system composed by Cr^{III} (S=3/2) ion and Cu^{II} (S=1/2) ion based on g=2.00. With the temperature decreasing, the $\chi_m T$ value increase slowly until about 50 K, and then, they increase rapidly to the maximum value of 3.07 emu·K·mol^{-1}. The $\chi_m T$ curve shows that the ferromagnetic interaction between Cr^{III} and Cu^{II} ions through cyanide group is weak ferromagnetic for complex **1**. The magnetic susceptibilities of complex **1** obey the Curie-Weiss law in the whole temperature range with the Weiss constant θ=1.70 (1) K and Curie constant C=

2.26(1) emu·K·mol^{-1}. The positive Weiss constant also supports the overall ferromagnetic interaction.

The field (H) dependence of magnetization (M) for complex **1** was measured in the field range from 0 to 50 kOe at T=2 K as shown in Fig.4. The field dependence of the magnetization of complex **1** is almost in agreement with their corresponding Brillouin curve for the S=2 spin state with g=2.00. However, the magnetization data are higher than the Brillouin curve deduced from an isolated Cr^{III} spin (S=3/2) and Cu^{II} spin (S=1/2) with g=2.00, further demonstrating
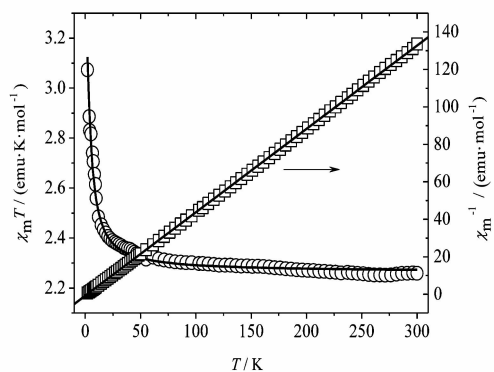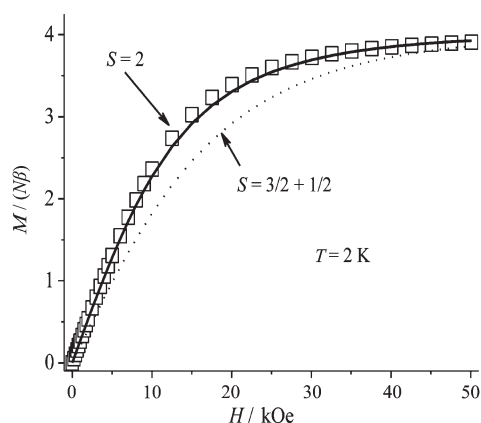

Fig.3　Temperature dependences of $\chi_m T$ for complex **1** measured under an applied field of 2 000 Oe

Solid or dotted line represent the Brillouin curve that corresponding to $S=2$ and $S=3/2+1/2$, respectively, with $g=2.0$

Fig.4　Field dependence of magnetization at $T=2$ K for complex **1**

that the slight ferromagnetic coupling exists in complex **1**.

To evaluate the magnetic coupling strength between the different metal ions of cyanide-bridged one-dimensional heterometallic complexes, the magnetic susceptibilities of this one-dimensional complex has been simulated by using MAGPACK program [31-33]. According to this method and on the basis of the crystal structure of complex **1** as discussed above, the one-dimensional complex **1** can be considered as a isotropic Heisenberg chain containing alternating spins 1/2 and 3/2 with two magnetic exchange interactions J_1 and J_2 (J_1 vs J_2 in Scheme 1). In this infinite single chain of complex 1, the magnetic susceptibilities can be simulated and calculated rationally and satisfactorily based on a closed eight members ring cluster model consisting of alternating spins 1/2 and 3/2 with two magnetic exchange interactions J_1 and J_2.
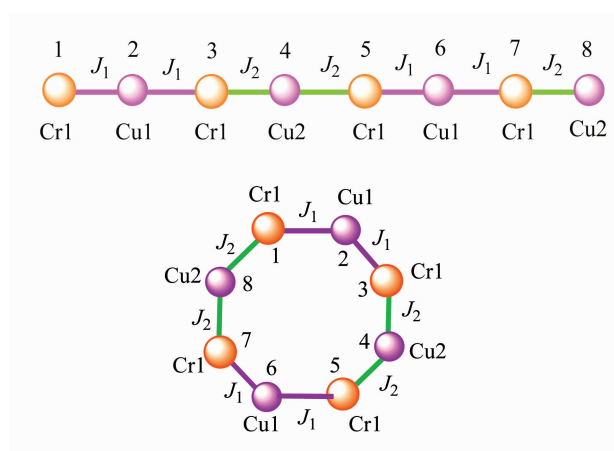
Scheme 1　Magnetic fitting model for complex **1**

According to this model, the magnetic susceptibilities in the 2~300 K temperature range for complex **1** was simulated, giving the best-fit parameters $J_1=0.72(1)$ cm^{-1}, $J_2=0.38(1)$ cm^{-1}, $g=2.006$ and $R=\sum (\chi_{obsd}T-\chi_{ald}T)^2/\sum (\chi_{obsd}T)^2=8.8\times10^{-5}$. The relatively small magnetic constants based on this model reveal that the magnetic coupling between Cr^{III} and Cu^{II} ions in complex **1** is weak ferromagnetic, which is reasonable and can be compared with those of most cyanide-bridged Cr^{III}-Cu^{II} complexes[34-35].

3　Conclusions

In summary, a cyanide-bridged Cr^{III}-Cu^{II} complex

has been synthesized based on [Cu(cyclam)](ClO_4)_2 and K[Cr(bpb)(CN)_2] building blocks. Single crystal X-ray diffraction analyses show that complex **1** has one-dimensional structure. Magnetic investigations indicate that the complex **1** exhibits a weak ferromagnetic coupling between Cr^{III} and Cu^{II} ions through the cyanide bridge, and the magnetic property is fitted based on a suitable theoretical model.

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