一维交替铁磁–反铁磁耦合的海森堡链[Mn(N₃)₂(pybox)]ₙ

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摘要:合成了一种叠氮锰一维链状化合物([Mn^{II}(N₃)₂(pybox)]ₙ,**1**),该化合物采用 2,6-吡啶双噁唑啉(pybox)三齿配体和叠氮作为共配体。用单晶 X 射线衍射的方法对其晶体结构进行了表征,结果表明二价锰离子通过双 *EO* 叠氮桥和双 *EE* 桥交替桥连成链状结构,其中锰离子分别与 4 个叠氮根和 1 个 pybox 配体上的 3 个氮原子配位,为七配位模式。变温磁化率数据表明,交替的 *EO* 叠氮桥和 *EE* 叠氮桥分别传递铁磁和反铁磁耦合相互作用形成一维交替的海森堡链。通过 *S*=5/2 交替铁磁–反铁磁耦合一维体系的理论模型,我们获得其磁耦合常数为:J_1=9.19 cm^{-1},J_2=−19.89 cm^{-1}。化合物 **1** 在低温表现出反铁磁有序。

关键词:叠氮;二价锰离子;海森堡链;磁性质
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One-Dimensional Alternating Ferromagnetic-Antiferromagnetic Coupled Heisenberg Chain [Mn^{II}(N₃)₂(pybox)]ₙ

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Abstract: We present here the structure and magnetism of the magnetic manganese-azido 1D chain compound of the type [Mn^{II}(N₃)₂(pybox)]ₙ (pybox=2,6-bis(4,5-dihydrooxazol-2-yl)pyridine), prepared by tridentate coligand pybox. In the structure, manganese(II) ions are alternatively bridged by double end-on azido ligands and double end-to-end azido ligands. Each Mn(II) cation possesses a seven coordination model, completed by three nitrogen atoms of one pybox ligand. The magnetic properties of this complex were systematically studied. The variable-temperature magnetic susceptibility data displays the existence of alternating ferro- and antiferromagnetic coupling through *EO* and *EE* azido bridges, respectively. The exchange parameters of J_1=9.19 cm^{-1} and J_2=−19.89 cm^{-1} were obtained by a theoretical model for an *S*=5/2 alternating ferromagnetic-antiferromagnetic coupled 1D system. Also, **1** exhibits antiferromagnetic ordering behavior at low temperature. CCDC: 943523.

Key words: azides; manganese(II) ion; Heisenberg chain; magnetic properties

0　Introduction

　　Recently, the construction of low-dimensional coordination polymers has attracted much attention in the field of molecular magnetism since the discovery of intriguing anisotropic systems with fascinating magnetic properties, such as single molecule magnets (SMMs) and single chain magnets (SCMs)[1]. Up to now, many 0D and 1D molecule-based magnetic materials have been reported, and the magnetic behavior has also been studied carefully[2-3]. In these magnetic molecule systems, it is important to select appropriate bridging ligands to transmit the exchange interactions between the paramagnetic centers effectively. Among the employed short bridging ligands with one to three atoms [3], such as O^{2-}, OH^-, CN^-, $HCOO^-$, NCS^-, N_2^-, $N_2N_5^-$, etc, have been employed[3], azide anion (N_3^-) is one of the most extensively used short bridges[4]. As a versatile bridging ligand, the azide anion could link two or more metal ions in various modes, for example, μ-1,1 [end-on (EO)], μ-1,3 [end-to-end (EE)], μ-1,1,1, μ-1,1,3, and so forth, which can give rise to a variety of interesting complicate structures. For azide bridging transition metal complexes, the magnetic interaction transmitted by azide anion has been studied both experimentally and theoretically. Generally, azide bridges can mediate ferromagnetic (FO) couplings in the EO mode and antiferromagnetic (AF) couplings in the EE mode[5].

　　Previous research demonstrated that the azide-metal complexes display very complicated and interesting magnetic properties because of their rich coordination modes. Besides bridging ligands, coligand can greatly determine the diversity of the coordination modes. For azide-transition metal system, several bidentate coligands, such as 2,2′-bipyridine (2,2′-bpy)[6], phenanthroline (phen)[7], 2,2′-bipyrimidine[8], 1,2-bis(4-pyridyl)ethane-*N*,*N*′-dioxide (bpeado)[9], and 2,2′-dipyridylamine (dpa)[10] et al, have been chosen to construct 1D magnetic coordination polymer chain. Compared with bidentate ligand, however, coligand with more than two ligand sites was seldom used. The pybox ligand [pyridine-2,6-bis(oxazoline)] is a type of tridentate ligands. This type of ligand was firstly wildly used as privileged chiral catalyst in asymmetric catalytic reaction[11]. Recently, the pybox ligand based rare earth complexes display novel luminescent properties[12]. Very recently, we have successfully synthesized a series of azide-copper complexes with new topologies[13]. As a continuation of preliminary work, we try to construct novel complexes of this series from pybox ligand with other transition metal ion. In this contribution, we present the crystal structure and magnetic properties for the [Mn(N₃)₂(pybox)]ₙ (pybox= 2,6-bis(4,5-dihydrooxazol-2-yl)pyridine) compound. The seven-coordinate Mn(Ⅱ) complex is 1D chain linked by double EO and double EE azide bridge alternatively. The magnetic exchange interactions between the Mn(Ⅱ) cations through the double EO and EE azide bridge are analyzed by a theoretical model for a ferromagnetic-antiferromagnetic $S=5/2$ chain.

1　Experimental

　　CAUTION! Azide salts are potentially explosive; such compounds should be synthesized and used in small quantities, and treated with the utmost care at all times.

1.1　Preparations of [Mn(N₃)₂(pybox)]ₙ (1)

　　Single crystals were obtained by diffusion. In a test tube, a MeOH/CH₂Cl₂ solution (5 mL, V_{MeOH}:$V_{CH_2Cl_2}$=10) of NaN₃ (26 mg, 0.4 mmol) and pybox ligand (2,6-bis(4,5-dihydrooxazol-2-yl)pyridine)[13] (43 mg, 0.2 mmol) was layered carefully with blank MeOH/CH₂Cl₂ solvent (5 mL, V_{MeOH}:$V_{CH_2Cl_2}$=20) in the middle and then a methanol solution (5 mL) of Mn(ClO₄)₂·6H₂O (74 mg, 0.2 mmol) at the top. The tube was sealed and undisturbed at room temperature for three days. Pale yellow plate-like crystals were obtained. Yield: 62 mg, 60%. Anal. Calcd. for C₁₁H₁₁MnN₉O₂(%): C, 37.09; H, 3.11; N, 35.39. Found (%): C, 37.05; H, 3.11; N, 35.41. IR (pure sample): ν=3 394 (w), 3 373 (w), 3 084 (w), 2 985 (w), 2 964 (w), 2 910 (w), 2 887 (w), 2 085 (s), 2 062 (s), 1 664 (w), 1 587 (m), 1 479 (w), 1 466 (w), 1 377 (w), 1 348 (w), 1 277 (w), 1 255 (m), 1 186 (w), 1 149 (w), 1 082 (w), 1 005 (w), 962 (w), 916 (w), 831 (w), 748 (w), 658 (w), 634 (w), 619 (w), 611 (w).

1.2 X-ray crystallography and physical measurements

The crystallographic data for the single crystal of compound **1** was collected at 173 K on a Saturn724+ CCD diffractometer with Confocal-monochromator Mo $K\alpha$ radiation (λ=0.071 073 nm). Intensities were collected using CrystalClear (Rigaku Inc., 2008) technique and absorption effects were collected using the multi-scan technique. The structure was solved by the direct method and refined by full matrix least-squares on F^2 using SHELXTL-97[14]. All the non-hydrogen atoms were refined using anisotropic thermal parameters. The detailed crystallographic parameters of compound **1** were listed in Table 1, selected bond lengths and angles in Table 2.

CCDC: 943523.

Powder X-ray diffraction (PXRD) data for compound **1** was collected in the range of 5°~60° for 2θ on crystalline sample using Rigaku Dmax 2000 diffraction with Cu $K\alpha$ radiation in flat-plate geometry at room temperature. The experimental PXRD pattern was compared with the calculated one of the single-crystal structure to identify the phase of the sample in the Fig.S1.

Elemental analyses of carbon, nitrogen and hydrogen were performed using an Elementar Vario

Table 1　Crystal data and structure refinement for 1

Compound	**1**	θ_{min}, θ_{max} / (°)	1.034 3, 27.483 2
Formula	$C_{11}H_{11}MnN_9O_2$	$F(000)$	724
Formula weight	356.23	Data collected	6 136
Crystal system	Monoclinic	Unique data	3 146
Space group	$P2_1/c$	Observed data ($I>2\sigma(I)$)	2 709
a / nm	0.890 6(2)	R_{int}	0.045 4
b / nm	1.968 8(5)	Number of parameters	208
c / nm	0.791 9(2)	$R_1^{[a]}$ ($I>2\sigma(I)$)	0.0542
β / (°)	94.15(4)	$wR_2^{[b]}$ ($I>2\sigma(I)$)	0.112 7
V / nm³	1.384 8(6)	$R_1^{[a]}$ (all data)	0.065
Z	4	$wR_2^{[b]}$ (all data)	0.119 3
D_c / (g·cm⁻³)	1.709	GOF	1.093
μ(Mo $K\alpha$) / mm⁻¹	0.981	$\Delta\rho^{[c]}$ /(e·nm⁻³)	+337, −345
Crystal size / mm	0.28×0.25×0.16	$\Delta/\sigma^{[d]}$, max., mean	0.000, 0.000
T_{max} and T_{min}	1.000 0, 0.617 7		

[a] $R_1= \sum \|F_o\|-\|F_o\|\| \sum \|F_o\|$; [b] $wR_2=[\sum w(F_o^2-F_c^2)^2 \sum w(F_o^2)^2]^{1/2}$; [c] Maximum and minimum residual electron density; [d] Maximum and mean sigma/shift.

Table 2　Selected bond lengths (nm) and angles (°) for 1

Mn(1)-N(1)	0.239 3(2)	Mn(1)-N(4)	0.234 8(2)	Mn(1)-N(9)#2	0.235 2(3)
Mn(1)-N(2)	0.242 2(2)	Mn(1)-N(4)#1	0.216 5(3)		
Mn(1)-N(3)	0.256 5(3)	Mn(1)-N(7)	0.216 7(3)		
N(4)#1-Mn(1)-N(7)	175.32(10)	N(7)-Mn(1)-N(1)	82.78(9)	N(1)-Mn(1)-N(2)	67.69(8)
N(4)#1-Mn(1)-N(4)	77.02(10)	N(4)-Mn(1)-N(1)	78.29(9)	N(4)#1-Mn(1)-N(3)	87.41(9)
N(7)-Mn(1)-N(4)	98.30(9)	N(9)#2-Mn(1)-N(1)	152.03(9)	N(7)-Mn(1)-N(3)	96.67(9)
N(4)#1-Mn(1)-N(9)#2	93.69(10)	N(4)#1-Mn(1)-N(2)	94.17(9)	N(4)-Mn(1)-N(3)	147.02(8)
N(7)-Mn(1)-N(9)#2	85.31(10)	N(7)-Mn(1)-N(2)	89.63(9)	N(9)#2-Mn(1)-N(3)	73.63(9)
N(4)-Mn(1)-N(9)#2	78.52(9)	N(4)-Mn(1)-N(2)	143.79(9)	N(1)-Mn(1)-N(3)	132.85(8)
N(4)#1-Mn(1)-N(1)	96.14(9)	N(9)#2-Mn(1)-N(2)	137.55(9)	N(2)-Mn(1)-N(3)	65.16(8)

Symmetry transformations used to generate equivalent atoms: #1 −x+1, −y+1, −z+2; #2 −x+1, −y+1, −z+1.

EL analyzer.

The FTIR spectrum was recorded against pure sample in the range of 4 000 to 600 cm^{-1} using a Nicolet iN10 MX Micro-infrared Spectrometer.

Magnetic measurement was performed on a MPMS XL-5 SQUID (Superconductivity Quantum Interference Device) magnetometer with crystalline sample fixed in a white capsule by parafilm. Diamagnetic corrections were estimated by using Pascal constants[15] and background c onnections by experimental measurements on sample holder.

2　Results and discussion

2.1　IR spectroscopy

For azido bridged compounds, the $\nu_{asym}(N_3)$ mode normally appeared as a very strong band in the range of 2 000~2 100 cm^{-1} in the IR spectrum. Compound **1** displays characteristic bands of the azide on the basis of the bridging modes (Fig.S2). In the region expected for $\nu_{as}(N_3^-)$ absorption, compound **1** exhibits two well-separated neighboring sharp and strong bands (2 085 cm^{-1} and 2 062 cm^{-1}), which is attributed to the presence of the two types of bridging modes of azide (2 062 cm^{-1} for double EO N$_3$ and 2 085 cm^{-1} for double EE N$_3$).

2.2　Crystal structure

Single-crystal X-ray structure determinations and powder X-ray diffraction (PXRD) analyses (see the Experimental Section and Fig.S1 in the Supporting Information) reveals that compound **1** crystallized in the monoclinic space group $P2_1/c$ (see Table 1). The crystal structure of **1** consists an azido-Mn(Ⅱ) neutral chain with alternative double EO-N$_3$ and double EE-N$_3$ bridges. The crystal structure of **1** and the coordination environment of Mn^{2+} in **1** are shown in Fig.1. There is only one crystallographically independent Mn^{2+} ion, which has a seven-coordination, completed by three nitrogen atoms of the pybox ligand (Mn1-N1 0.239 3(2) nm, Mn1-N2 0.242 2(2) nm, Mn1-N3 0.256 5 nm), two nitrogen atoms of EO-N$_3$ (Mn1-N4 0.234 8(2) nm, Mn1-N4#1 0.216 5(3) nm; symmetry code #1: $-x+1$, $-y+1$, $-z+2$), and two nitrogen atoms of EE-N$_3$ (Mn1-N7 0.216 7(3) nm, Mn1-N9#2 0.235 2(3) nm; symmetry code #2: $-x+1$, $-y+1$, $-z+1$). Five nitrogen

atoms (N1, N2, N3, N4, and N9#2) form the approximate basal phase and two other nitrogen atoms (N4#2, N7) are bonded in the axial direction. The EO and EE azide bridges are arranged perpendicular to each other. Because of the existence of an inversion center, the Mn-N4-Mn#1-N4#1 bridging unit forms a plane. The EO bridging azides are approximately linear with the N4-N5-N6 angle being 178.94(31)°. The Mn1-N4-Mn1#1 angle in the EO mode is 102.97(10)°. This is consistent with the structural results usually obtained with the other EO azide-bridging complexes[6a,9]. For the EE azide bridges, the Mn1-N7-N8 angle is 126.02(20)° and Mn1-N9#2-N8#2 angle is 135.42(20)°, forming a chair configuration of the Mn-(N$_3$)$_2$-Mn unit and a torsion angle of 155.28(21)°. The intrachain Mn⋯Mn distances are 0.353 3(1) and 0.555 3(1) nm in the EO and EE bridges, respectively.

The three rings in pybox ligand are approximately coplanar. In the crystal, the pybox ligands stack parallel to each other (see Fig.2). The pairs of pybox ligands from two neighboring chains
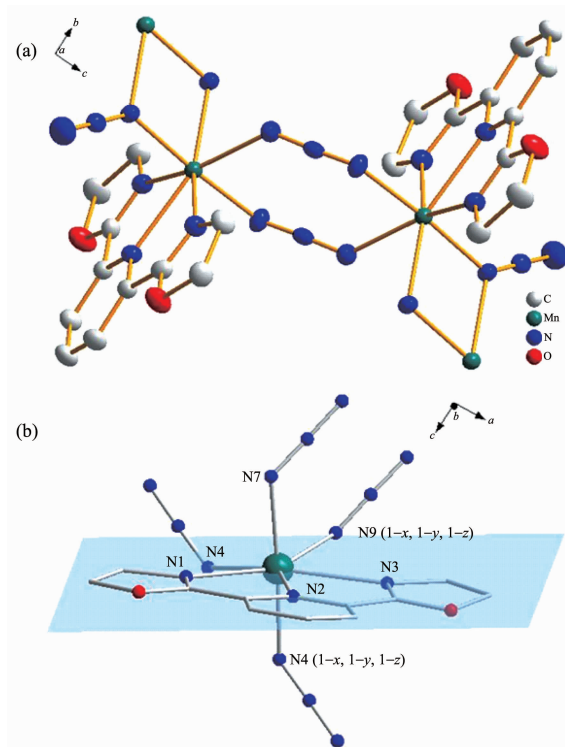
Ellipsoid probability for non-hydrogen atoms is 50%; Hydrogen atoms are omitted for clarity

Fig.1　(a) Structure unit of compound **1**, (b) Coordination environment of Mn^{2+} in **1**

overlapped with the distance approximately 0.342 6(3) nm, implying the existence of π-π stacking through the pybox ligand.
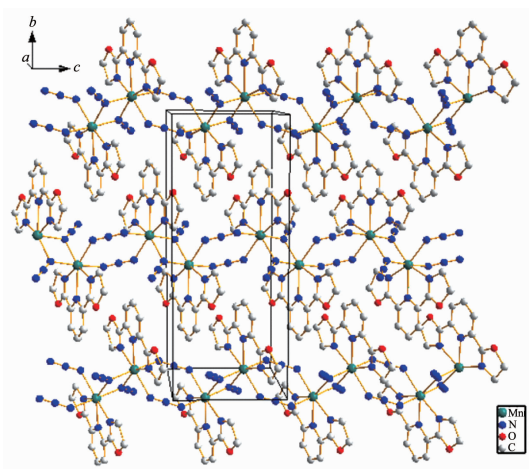

Fig.2　Arrangement of the chains in the bc plane

2.3　Magnetic properties

The magnetic measurements were performed on polycrystalline samples of **1** using Quantum-Design MPMS magnetometer. Variable-temperature magnetic susceptibility measurement was performed from 2 to 300 K. The $\chi_M T$ versus T plot of **1** under an applied field of 1 kOe is shown in Fig.3　(χ_M is the molar magnetic susceptibility per Mn^{2+} ion). The $\chi_M T$ value at room temperature is equal to 4.27 $cm^3 \cdot mol^{-1} \cdot K$, which is slightly lower than that expected for an uncoupled Mn^{2+} ion ($\chi_M T$=4.38 $cm^3 \cdot mol^{-1} \cdot K$ for an $S=5/2$ ion with $g=2$)[16]. The $\chi_M T$ value decreases continu-ously upon cooling　(see Fig.3). The magnetic susce-ptibility data in the range of 70~300 K obeys the Curie-Weiss law, $\chi_M = C/(T-\theta)$. The linear fitting of the χ_M^{-1} versus T plots gives the Curie constant C =4.76 $cm^3 \cdot mol^{-1} \cdot K$ and Weiss constant θ =−32.53 K (see Fig.3). The negative Weiss value indicates the overall antiferromagnetic (AF) coupling. The χ_M value increases upon cooling, reaching a maximum value of 0.057 $cm^3 \cdot mol^{-1}$ at 28 K, then drops at low temperatures. The peak suggests the presence of possible antiferro-magnetic (AF) ordering in this compound (see Fig.4). The Néel temperature, T_N, determined from sharp peak of d($\chi_M T$)/dT, is 19.0 K (see inset of Fig.4)[17-19]. The ratio of $T_N/T_{\chi_{M,max}}$ =0.68 for **1** does show the low-dimensional AF ordering character[20]. The field depen-

dence of the magnetization of **1** measured at 1.8 K increases linearly with the increased dc field. The molar magnetization at 50 kOe is only 0.51$N\beta$ (the unit of magnetization)　(see Fig.S3), far from the saturation value (5$N\beta$ for S=5/2 when g factor is taken equal to 2.00). This is important evidence that the AF ordering exists in compound **1**.
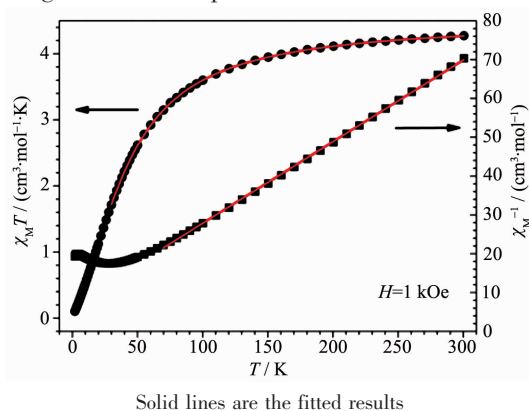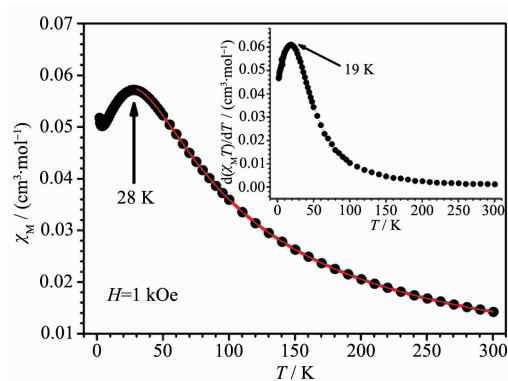

Solid lines are the fitted results

Fig.3　Plots of temperature dependence of $\chi_M T$ and χ_M^{-1} under 1 kOe dc field of **1**

Solid line is the fitted results; Inset: d($\chi_M T$)/dT vs T

Fig.4　Temperature dependence of χ_M

According to the reported experimental and theoretical result, complex **1** with alternative double EO-N_3 and double EE-N_3 bridges should exhibit alternating ferro- and antiferromagnetic coupling interaction[5]. Normally, the double EO bridges transfer ferromagnetic interactions between Mn(Ⅱ) center and the double EE bridges mediate antiferromagnetic interaction[6a]. So we propose the magnetic behavior of **1** should be considered as two alternating exchange constants: a positive J_1 for EO N_3 bridges and a negative J_2 for EE bridges.

Rojo et al reported a Mn(Ⅱ)-azido one-dimensio-

nal compound with $[Mn(bipy)(N_3)_2]_n$ (bipy=2,2′-bipyridine) [6a]. This compound also consists a 1D chain structure with alternative double EO-N_3 and double EE-N_3 bridges. The difference between the two compounds is just the coligand used. Considering the similar topology of two compounds, the similar theoretical model for a ferromagnetic-antiferromagnetic $S = 5/2$ chain can be used to fit the coupling constant of compound **1**[21-22]. The alternating chain with nearest neighbor exchange interactions can be described by the spin Hamiltonian: $H=-J_1S_{2i}S_{2i+1}-J_2S_{2i+1}S_{2i+2}$, in which J_1 and J_2 is the alternating exchange constants and S stand for spin vector of each magnetic unit. The manganese(II) ion exhibits a large spin with $S=5/2$. The magnetic susceptibility could be expressed as:

$$\chi=\frac{Ng^2\mu_B^2}{3kT}\left(\frac{1+u_1+u_2+u_1u_2}{1-u_1u_2}\right) \tag{1}$$

where $u_1=\coth[J_1/(kT)]-kT/J_1$ and $u_2=\coth[J_2/(kT)]-kT/J_2$, N is Avogadro number, g is gyromagnetic factor, β is Bohr magneton, and k is Boltzmann constant. Equation (**1**) was used to fit the $\chi_M T$ data of compound **1**. The best fitting parameters　(above 30 K) are $J_1=$ 9.19 cm⁻¹, $J_2=-19.89$ cm⁻¹, $g=2.02$, and $R=2.91\times10^{-4}$ for **1** (R is defined as $\sum[(\chi_M T)_{obs}-(\chi_M T)_{calcd}]^2/\sum[(\chi_M T)_{obs}]^2$). The antiferromagnetic coupling constant J_2 is greater than ferromagnetic coupling constant J_1, so the antiferromagnetic interaction is dominant in this 1D chain.

3　Conclusion

In summary, the structure and magnetism of the magnetic manganese-azido 1D chain compound of the type $[Mn^{II}(N_3)_2(pybox)]_n$, prepared by tridentate co-ligand pybox, were systematically studied. In this 1D chain structure, manganese(II) ions are alternatively bridged by double end-on azido ligands and double end-to-end azido ligands and each Mn(II) cations possess a novel seven coordination. The variable-temperature magnetic susceptibility data displays the existence of alternating ferro- and antiferromagnetic coupling through EO and EE azido bridges, respectively. The exchange parameters of $J_1=9.19$ cm⁻¹ and $J_2=-19.89$ cm⁻¹ were obtained by a theoretical model for an $S=5/2$ alternating ferromagnetic-antiferromagnetic coupled 1D system.

This compound demonstrates that tridentate coligand can also be used to construct 1D azido bridging magnetic chain. Our result will enrich the azido magnetic chains system. The synthesis and magnetism of new coordination polymers from pybox ligand are in progress.

Supporting Information: The PXRD, IR, magnetic data, and crystal structure were included. This information is available free of charge via the internet at http://www.wjhxxb.cn.

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