

基于含双吡唑的四羧酸配体构筑的Fe(II)/Co(II) 同构配合物的合成、晶体结构及磁性质

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摘要: 本文报道了2种二维同构配位聚合物 $\{(\text{NH}_2(\text{CH}_3)_2)[\text{M}(\text{L})]\}_n$ ($\text{M}=\text{Fe}$ (1), Co (2), $\text{H}_4\text{L}=1, 1'-(1, 4\text{-苯基双(亚甲基)双}(1H\text{-吡唑-3, 5-二羧酸}))$)的合成、晶体结构和磁性。X射线单晶衍射结构分析表明, 2种配合物属于相同的单斜晶系 $P2_1/n$ 空间群, 中心金属离子 M(II) 是六配位的八面体构型。该配合物的特点是配离子带有2个负电荷, 溶剂DMF分解形成的二甲基胺离子作为阳离子而使配合物保持电中性。在聚合物中, 每个配体通过吡唑环上的N、O原子和该吡唑环上的单齿O原子桥联2个金属离子, 形成 $\cdots\text{M-L-M-L}\cdots$ 一维链, 此一维链相交形成包含 M_4L_4 单元的无限二维网络结构。磁性研究表明, 配合物1和2具有反铁磁性。

关键词: 晶体结构; 1, 1'-(1, 4-苯基双(亚甲基)双)(1H-吡唑-3, 5-二羧酸); 铁(II)配合物; 钴(II)配合物; 磁性; 配位聚合物

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Synthesis, Structural and Magnetic Characterization of Fe(II)/Co(II) Isomorphous Complexes Based on a Dipyrazole-Containing Tetracarboxylate Ligand

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Abstract: We herein report the synthetic, structural, and magnetic studies on two 2D isomorphous complexes, $\{(\text{NH}_2(\text{CH}_3)_2)[\text{M}(\text{L})]\}_n$ ($\text{M}=\text{Fe}$ (1), Co (2), $\text{H}_4\text{L}=1, 1'-(1, 4\text{-phenylenebis(methylene)bis}(1H\text{-pyrazole-3, 5-dicarboxylic acid}))$). From single crystal X-ray crystallography, it is found that the complexes crystallized in the same space group monoclinic $P2_1/n$ and have six-coordinate octahedron structures. The framework features anionic having a -2 charge, and the electroneutrality is achieved by the incorporation of the protonated dimethylamine by hydrolysis of DMF in the voids of the net. In the two polymers, each ligand bridges two metal(II) ions through cheating N, O atoms of the pyrazole ring and monodentate O atoms of the same pyrazole ring, forming $\cdots\text{M-L-M-L}\cdots$ chains and the 1D chains intersect to form an infinite 2D network which contains nearly square M_4L_4 units. Magnetic susceptibility measurements indicate the presence of antiferromagnetic properties in complexes 1 and 2. CCDC: 1923316, 1; 1923318, 2.

Keywords: crystal structure; 1, 1'-(1, 4-phenylenebis(methylene)bis)(1H-pyrazole-3, 5-dicarboxylic acid); Fe(II) complex; Co(II) complex; magnetic properties; coordination polymers

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0 Introduction

The prudent design of coordination polymers (CPs) by connecting the metal ions as single point nodes or secondary building units (SBU) with a variety of organic ligands as linkers has attracted immense interest in the past few decades^[1]. This is not only due to their fascinating network structures and novel functionalities but also due to the ease of tuning such structures with the change of linkers and metals. It has been observed CPs have great potential for multiple applications depending on their structure, chemical composition, particle size, *etc.* Thus, in the last decades, CPs have demonstrated usefulness in fields such as hydrogen and methane storage capture^[2], separation of CO₂^[3], water adsorption^[4], solvent sponge behavior^[5], controlled drug entrapment and release^[6], heterogeneous catalysis^[7], and luminescence^[8]. While many of these applications are based on the framework porosity, CPs materials also exhibit physical properties traditionally associated with highly dense oxide systems. For example, CPs may also have interesting magnetic properties because the magnetic metal ions and their coupling can be tailored in the CP structure through the incorporation of magnetic moment carriers such as paramagnetic metals, open-shell organic ligands, or both^[9]. So the designed syntheses of CPs having attractive magnetic properties are immensely important among the ever-growing number of functional applications. Such a class of compounds was investigated to design magnetic materials because magnetic coupling can easily be tuned and controlled by altering the linkers and nodes^[10-13]. Side by side it is also very important to understand the magnetic exchange pathway to rationalize the exact design of magnetically functional CPs.

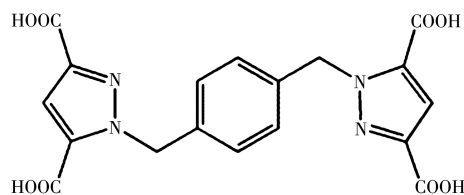
As magnetism is a cooperative phenomenon, a connection between moment carriers at distances within the interacting range is necessary; carboxylic-based and nitrogen-based ligands have proved to have good superexchange pathways for magnetic couplings^[14]. Especially, the carboxylate-based bridging ligand is one of the very popular choices for the execution of magnetic CPs. Thus, coordination architectures having

carboxylate-donating linkers and paramagnetic metal ions have attracted the attention of contemporary research for understanding the magnetic exchange through the OCO bridges of the carboxylate ligands which show versatile binding abilities. In addition, flexible diamagnetic ligands are usually used to link magnetic *d*- or *f*-block metal ions into extended networks, facilitating magnetic exchange in one, two, and three dimensions^[15-16]. Paramagnetic transition metal elements allow the variation of spin quantum number and magnetic anisotropy, two important parameters in magnetism. Among these elements, Co(II) and Ni(II) appear as the preferred choice to develop magnetic CPs, because it provides the highest magneto-crystalline anisotropy, which results in record magnetic hardness^[17].

In the CPs, there are self-assemblies of isomorphous or isotopologue compounds, which provide variations of magnetic anisotropy and spin quantum numbers that affect the magnetic behavior of such isomorphous systems, such as [M(L)₂(CH₃OH)₂] (M=Mn(II), Fe(II), and Co(II), HL=2,6-bis(pyrazole-1-yl)pyridine-4-carboxylic acid), M(HCOO)₂(4,4'-bpy)·*n*H₂O (M=Co(II) and Ni(II)); [M(L)(N₃)₂]·3*n*H₂O (M=Mn(II), Co(II), and Ni(II), L⁻=1-(4-carboxylatobenzyl-pyridinium-4-carboxylate), and [M(H₂bpta)]_n (H₄bpta=2,2',4,4'-biphenyltetracarboxylic acid, M=Fe(II), Ni(II), Cu(II), and Zn(II))^[18-20]. The magnetic interactions between transition metal centers usually are mainly mediated through M-L-M super-exchange which is important in magnetic orbits of metal ions, in which the *nd*-orbits of metal ions are combined out of phase with the *np*-orbits of ligands. The orbital interaction plays a significant role in the spin Hamiltonian for a given magnetic system. Indeed, a substantial number of CPs with magnetic properties have been reported, due to the use of constitutive open-shell transition metal ions within the framework of the structure.

With this in mind, we selected a ligand 1,1'-(1,4-phenylenebis(methylene))bis-(1*H*-pyrazole-3,5-dicarboxylic acid) (H₄L, Scheme 1), succeeded in obtaining two new isomorphous 2D complexes {(NH₂(CH₃)₂)₂[Fe(L)]}_n (**1**) and {(NH₂(CH₃)₂)₂[Co(L)]}_n (**2**), and analyzed magnetic properties of the two complexes. The result of

variable-temperature magnetic measurements exhibits antiferromagnetic exchange interactions in complexes **1** and **2**.



Scheme 1 Structure of H_4L

1 Experimental

1.1 General methods and materials

H_4L was purchased from Jinan Henghua Science & Technology Co., Ltd., China. All solvents and other reagents were commercially available and were used without further purification. Fourier transform (FT) IR spectra were taken on a BRUKER TENSOR27 spectrometer in a 4 000-400 cm^{-1} region with KBr pellets. Elemental analyses of C, H, and N were recorded on a CHNO - Rapid instrument. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda=0.154\ 18\ nm$) and the data were recorded within a 2θ range of 5° - 50° . The working voltage and current were 60 kV and 50 mA, respectively. The calculated PXRD patterns were generated from the single-crystal X-ray diffraction data using PLATON software. Magnetic susceptibility data were obtained with a SQUID magnetometer (Quantum MPMS-VSM) in a temperature range of 1.8-300.0 K by using an applied field of 2 000 Oe. The magnetic susceptibility data were corrected for the diamagnetism of the samples using Pascal constants. Thermogravimetric analyses (TGA) were carried out with a Dupont thermal analyzer in a temperature range of 25-800 $^\circ C$ under an N_2 flow with a heating rate of $5\ ^\circ C\cdot min^{-1}$.

1.2 Preparation of complexes **1** and **2**

A mixture of H_4L (20.7 mg, 0.05 mmol), $FeSO_4\cdot 7H_2O$ (27.8 mg, 0.10 mmol), $SnCl_2\cdot 2H_2O$ (11.3 mg, 0.05 mmol), and 10 mL of mixed solvents (acetonitrile/DMF/water, 3:3:4, V/V) was placed in a 15 mL Teflon-lined stainless steel autoclave. The mixture was heated under autogenous pressure at 160 $^\circ C$ for 72 h and then

cooled to room temperature naturally. Red block-shaped crystals of **1** were collected by filtration, washed with H_2O , and dried in the air. Yield: 70%. Anal. Calcd. for $C_{22}H_{26}FeN_6O_8$ (%): C 47.1, H 4.63, N 14.9; Found(%): C 47.2, H 4.66, N 14.8. IR (KBr, cm^{-1}): 3 437s, 3 130w, 1 605s, 1 533m, 1 476m, 1 362s, 1 277m, 1 241m, 1 106w, 1 013s, 821s, 785w, 764m, 543m.

The preparation process of complex **2** was the same as that of **1**, except that $FeSO_4\cdot 7H_2O$ and $SnCl_2\cdot 2H_2O$ were replaced by $CoCl_2\cdot 3H_2O$ (23.8 mg, 0.10 mmol). Pink block-shaped crystals of **2** were collected, washed with H_2O , and dried in air. Yield: 70%. Anal. Calcd. for $C_{22}H_{26}N_6CoO_8$ (%): C 47.0, H 4.63, N 15.0; Found(%): C 46.8, H 4.64, N 14.8. IR (KBr, cm^{-1}): 3 419w, 2 802w, 2 399w, 1 922w, 1 610s, 1 525m, 1 487m, 1 355s, 1 274m, 1 245m, 1 107w, 1 024s, 837s, 792w, 767m, 550m.

1.3 X-ray crystallography

The data for complex **1** were collected using a SuperNova (Cu) X-ray Source diffractometer utilizing Cu $K\alpha$ ($\lambda=0.154\ 18\ nm$) radiation at 173(2) K. Single-crystal X-ray diffraction data for complex **2** were collected in the Beijing Synchrotron Radiation Facility (BSRF) beamline 3W1A, which were mounted on a MARCCD-165 detector ($\lambda=0.071\ 00\ nm$) with the storage ring working at 2.5 GeV. In the process, the crystal was protected by liquid nitrogen at 100(2) K. Data was collected by the program MARCCD and processed using HKL 2000.

All the structure was solved by direct methods employed in the program SHELXS-2014 and refined by full-matrix least-squares methods against F^2 with SHELXL-2016. The determination of cell parameters and data reduction was performed with SAINT Plus. Program SADABS was used for absorption corrections. After all non-H atoms were refined anisotropically, hydrogen atoms attached to C atoms were placed geometrically and refined using a riding model approximation, with a C—H length of 0.093 nm and $U_{iso}(H)=1.2U_{eq}(C)$. A summary of the crystallographic data and data collection and refinement parameters for both complexes are listed in Table 1.

CCDC: 1923316, **1**; 1923318, **2**.

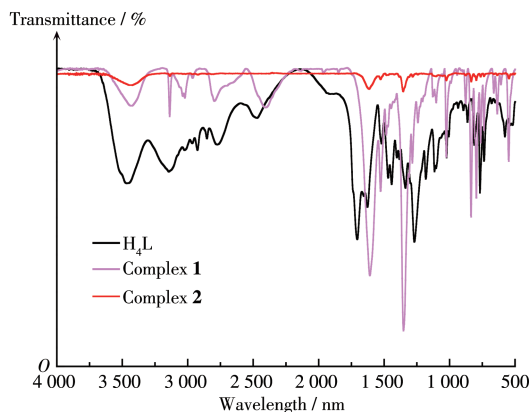
Table 1 Crystal data and structure refinement parameters for complexes **1** and **2**

Parameter	1	2
Formula	C ₂₂ H ₂₆ FeN ₆ O ₈	C ₂₂ H ₂₆ CoN ₆ O ₈
Formula weight	558.34	561.42
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / nm	1.111 34(7)	1.096 5(2)
<i>b</i> / nm	1.051 25(4)	1.051 9(2)
<i>c</i> / nm	1.175 45(8)	1.178 6(2)
β / (°)	117.074(8)	116.43(3)
<i>V</i> / nm ³	1.222 7(15)	1.217 3(5)
<i>Z</i>	2	2
<i>D_c</i> / (g·cm ⁻³)	1.516	1.532
μ / mm ⁻¹	5.474	0.765
<i>F</i> (000)	580	582
GOF	1.094	1.002
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.044 9	0.028
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.128 8	0.103

2 Results and discussion

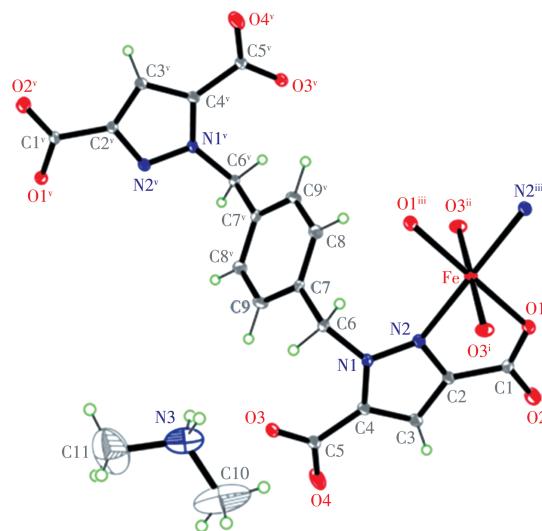
2.1 IR characterization

The peaks of FT-IR indicate that the strong broad absorption bands in the range between 3 419 cm⁻¹ should be assigned to the characteristic vibrations of the $\nu_{\text{N-H}}$ stretching frequencies. The absence of strong bands around 1 706 cm⁻¹ in the FT-IR spectra indicates that —COOH group has been completely deprotonated to generate L⁴⁻ anions, which is in agreement with that from its X-ray single crystal structure, and the characteristic strong bands of the coordinated carboxylate groups appeared at 1 610-1 525 cm⁻¹ for the asymmetric stretching and 1 355-1 274 cm⁻¹ for the symmetric one (Fig.1).

**Fig.1** FT-IR spectra of H₄L and complexes **1** and **2**

2.2 Description of crystal structures

Since the two complexes are isomorphous, only the structure of complex **1** will be described here. Complex **1** crystallizes in the *P*2₁/*n* space group containing the anion framework. The asymmetric unit consists of a half Fe²⁺ ion, a half of a fully deprotonated L⁴⁻ ligand, and one non-coordinated protonated dimethylamine cation by hydrolysis of DMF (Fig.2). As can be deduced

**Fig.2** Atom labels and coordination environments of the Fe(II) ions in complex **1** with displacement ellipsoids drawn at the 30% probability level

from the charge balance, the framework is anionic having a -2 charge, and the electroneutrality is achieved by the incorporation of the protonated amine in the voids of the net. In complex **1**, the Fe(II) ion is surrounded by four oxygen atoms ($O1$, $O1^{iii}$, $O3^i$, $O3^{ii}$) from four L^{4-} ions and two nitrogen atoms ($N2$, $N2^{iii}$) of two different L^{4-} ions to present an octahedron geometry where the *cis*- and *trans*-angles separate at the metal is $76.65(8)^\circ$ - 180.0° . The Fe—O and Fe—N bond lengths are in a range of $0.206\ 3(2)$ - $0.216\ 5(2)$ nm and $0.216\ 7(2)$ nm, respectively, which are slightly shorter than those of Fe(II) complexes^[21]. The bond lengths

(M—O and M—N) for the two complexes decrease with the increase of the *d*-electronic number, in agreement with the radius variation of the metal ions (Table 2).

As shown in Fig. 3a, in complex **1**, two carboxyl groups of pyrazole are fully deprotonated, each ligand bridges two Fe(II) ions through chelating N, O atoms of the pyrazole ring and monodentate O atom of the same pyrazole ring, forming $\cdots\text{Fe-L-Fe-L}\cdots$ chains parallel to the crystallographic *b* direction. The Fe $\cdots$ Fe distance separated by a $\mu_{1,5}$ -pyrazole-carboxylate bridge is $0.795\ 7(1)$ nm (Co $\cdots$ Co $0.798\ 0(2)$ nm for **2**). The dihedral angle between the planes of the benzene ring and

Table 2 Selected bond distances (nm) and angles ($^\circ$) around metal centers in isomorphous polymers **1** and **2**

1 (173 K)					
Fe1—O3 ⁱ	0.206 3(2)	Fe1—O3 ⁱⁱ	0.206 3(2)	Fe1—O1 ⁱⁱⁱ	0.216 5(2)
Fe1—O1	0.216 5(2)	Fe1—N2	0.216 7(2)	Fe1—N2 ⁱⁱⁱ	0.216 7(2)
O3 ⁱ —Fe1—O3 ⁱⁱ	180.0	O3 ⁱ —Fe1—O1 ⁱⁱⁱ	88.51(8)	O3 ⁱⁱ —Fe1—O1 ⁱⁱⁱ	91.49(8)
O3 ⁱ —Fe1—O1	91.49(8)	O3 ⁱⁱ —Fe1—O1	88.51(8)	O1 ⁱⁱⁱ —Fe1—O1	180.0
O3 ⁱ —Fe1—N2	92.48(9)	O3 ⁱⁱ —Fe1—N2	87.52(9)	O1 ⁱⁱⁱ —Fe1—N2	103.35(8)
O1—Fe1—N2	76.65(8)	O3 ⁱ —Fe1—N2 ⁱⁱⁱ	87.52(9)	O3 ⁱⁱ —Fe1—N2 ⁱⁱⁱ	92.48(9)
O1 ⁱⁱⁱ —Fe1—N2 ⁱⁱⁱ	76.65(8)	O1—Fe1—N2 ⁱⁱⁱ	103.35(8)	N2—Fe1—N2 ⁱⁱⁱ	180.0
2 (100 K)					
Co1—O1	0.207 53(11)	Co1—O1 ⁱ	0.207 53(11)	Co1—O3 ⁱⁱ	0.209 60(11)
Co1—O3 ⁱⁱⁱ	0.209 60(11)	Co1—N2 ⁱⁱ	0.213 59(13)	Co1—N2 ⁱⁱⁱ	0.213 59(13)
O1—Co1—O1 ⁱ	180.0	O1—Co1—O3 ⁱⁱ	91.48(5)	O1 ⁱ —Co1—O3 ⁱⁱ	88.52(5)
O1—Co1—O3 ⁱⁱⁱ	88.52(5)	O1 ⁱ —Co1—O3 ⁱⁱⁱ	91.48(5)	O3 ⁱⁱ —Co1—O3 ⁱⁱⁱ	180.00(5)
O1—Co1—N2 ⁱⁱ	93.12(5)	O1 ⁱ —Co1—N2 ⁱⁱ	86.88(5)	O3 ⁱⁱ —Co1—N2 ⁱⁱ	78.28(5)
O3 ⁱⁱⁱ —Co1—N2 ⁱⁱ	101.72(5)	O1—Co1—N2 ⁱⁱⁱ	86.88(5)	O1 ⁱ —Co1—N2 ⁱⁱⁱ	93.12(5)
O3 ⁱⁱⁱ —Co1—N2 ⁱⁱⁱ	101.72(5)	O3 ⁱⁱⁱ —Co1—N2 ⁱⁱⁱ	78.28(5)	N2 ⁱⁱ —Co1—N2 ⁱⁱⁱ	180.0

Symmetry codes: ⁱ $x-1/2, -y+3/2, z-1/2$; ⁱⁱ $-x+1/2, y+1/2, -z+1/2$; ⁱⁱⁱ $-x, -y+2, -z$; ^{iv} $-x+1/2, y-1/2, -z+1/2$; ^v $-x, -y+1, -z$ for **1**; ⁱ $-x+1, -y+1, -z$; ⁱⁱ $x-1/2, -y+1/2, z-1/2$; ⁱⁱⁱ $-x+3/2, y+1/2, -z+1/2$; ^{iv} $-x+2, -y+1, -z+1$; ^v $-x+3/2, y-1/2, -z+1/2$ for **2**.

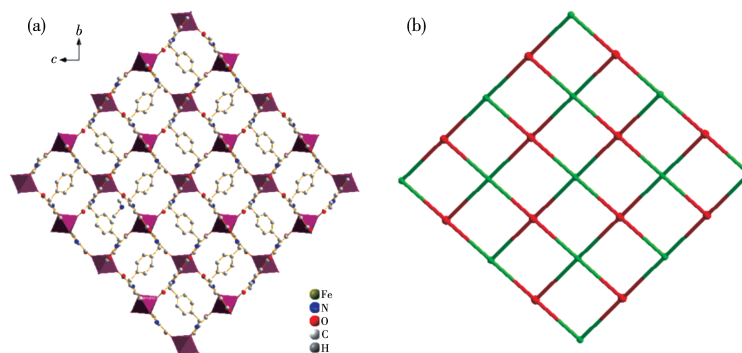


Fig. 3 (a) Two-dimensional sheets extending in the *b*-axis and *c*-axis of complex **1**;
(b) Topology net of complex **1** with Schläfli symbol $\{3^{12}.4^{14}.5^2\}$

pyrazole rings is $71.07(3)^\circ$. The 1D chains intersect to form an infinite 2D network that contains nearly square Fe_4L_4 units. For each unit, four L^{4-} anions act as the four edges, and four Fe(II) ions represent the four vertices. The lengths of the diagonals are 1.051 3 and 1.194 8 nm, compared to 1.060 9 and 1.200 4 nm for **2**, and the interior angles are 82.68° and 97.32° , compared to 82.46° and 97.54° for **2**.

From the topological point of view, the frameworks of complexes **1** and **2** can be simplified by the application of a (4,4)-connected topological approach (Fig.3b) using TOPOS^[22]. Each ligand is linked to four Fe^{2+} ions to act as a 4-connected node; each Fe^{2+} ion is bound by four L^{4-} ions to act as a 4-connected node. The topological notation is $\{3^{12}.4^{14}.5^2\}$ from TOPOS program analysis.

To confirm that the phase of the bulk sample is pure and the crystal structures of **1** and **2** are truly representative of the bulk material, the PXRD experiments were carried out. As shown in Fig.4, PXRD pat-

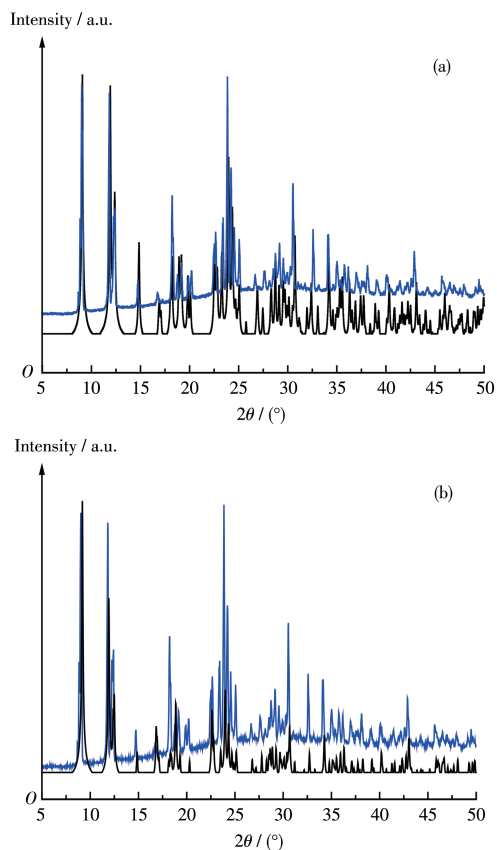


Fig.4 Simulated (bottom) and experimental (top) PXRD patterns of complexes **1** (a) and **2** (b)

terns of **1** and **2** were determined at room temperature, which matched well with those simulated from their X-ray single crystal diffraction data, and the high purity of the complexes can be confirmed. In addition, TGA results indicate that complexes **1** and **2** were stable until about 604 K (Fig.5).

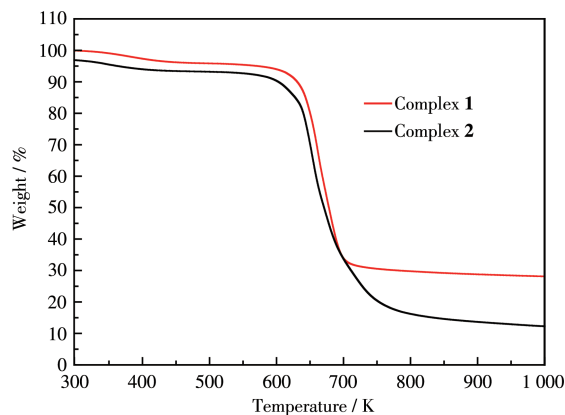


Fig.5 TGA curves for complexes **1** and **2**

2.3 Magnetic properties

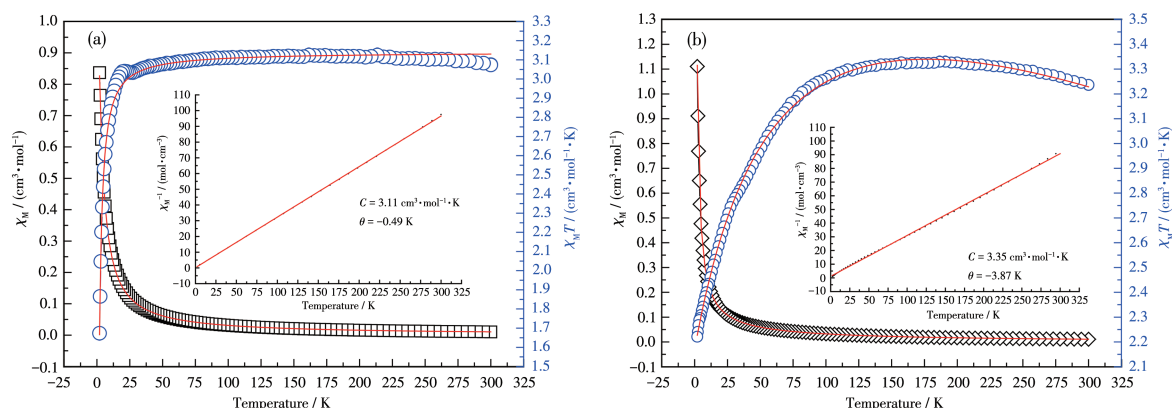
To gain insight into magnetic changes in isomorphous polymers, magnetic measurements were carried out on the well-crushed crystalline samples. Variable-temperature magnetic susceptibilities of the two complexes were measured in a temperature range of 1.8–300.0 K with an applied magnetic field of 2 000 Oe.

As shown in Fig.6a, the $\chi_{\text{M}}T$ value of **1** ($3.07 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$) at 300.0 K was larger than the spin-only $\chi_{\text{M}}T$ of $3.00 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ expected for a single isolated high-spin Fe(II) ion ($g=2.0$ and $S=2$). Upon cooling, the $\chi_{\text{M}}T$ value decreased smoothly and reached a minimum of $1.67 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2.0 K, which indicates a characteristic feature of antiferromagnetic coupling between Fe(II) ions. The Curie-Weiss fit, namely $\chi=C/(T-\theta)$, in the range of 1.8 to 300.0 K afforded a Curie constant of C being $3.11 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ and a Weiss constant of θ being -0.49 K (Fig.6a, Inset).

To further investigate the magnetic properties of **1**, the data can be fitted upon 7.0 K by an expression (Eq.1) for $S=2$ systems^[23]:

$$\chi_{\text{M}} = \frac{2N\beta^2 g^2}{kT} \frac{e^{2J/(kT)} + 5e^{6J/(kT)} + 14e^{12J/(kT)} + 30e^{20J/(kT)}}{1 + 3e^{2J/(kT)} + 5e^{6J/(kT)} + 7e^{12J/(kT)} + 9e^{20J/(kT)}} \quad (1)$$

where J is the coupling constant between the neighboring Fe(II) ions; N is Avogadro's number; β is the Bohr



The red solid line represents the best fit

Fig.6 Temperature dependence of $\chi_M T$ and $1/\chi_M$ collected in an applied field of 2 000 Oe for complexes **1** (a) and **2** (b)

magneton; k is the Boltzmann constant; g is the Lande value.

The best fit well reproduced the experimental data over the entire temperature range with $g=1.95$, $J=-0.181 \text{ cm}^{-1}$ with an agreement factor (R) of 5.7×10^{-4} , where $R = \sum (\chi_M T_{\text{exp}} - \chi_M T_{\text{cal}})^2 / \sum (\chi_M T_{\text{exp}})^2$. The negative θ and J values indicate the presence of weak antiferromagnetic interaction between adjacent Fe(II) ions.

According to the literature^[24], it can be deduced that the unpaired spin in e_g orbitals favor ferromagnetic interactions, whereas those in t_{2g} orbitals favor stronger antiferromagnetic interactions, with only one unpaired electron in a t_{2g} orbital being enough to dominate the overall superexchange. Therefore, Fe (II) complexes should show antiferromagnetic. Our result is in good

agreement with these expectations^[25].

As shown in Fig.6b, the $\chi_M T$ value of **2** ($3.23 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$) at 300.0 K was larger than the spin-only value ($1.88 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, $g=2.0$ and $S=3/2$). Upon cooling, the $\chi_M T$ value slightly increased first, then decreased and reached $2.22 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2.0 K, which indicates a characteristic feature of antiferromagnetic coupling between Co(II) ions. The magnetic susceptibility obeys the Curie-Weiss law with a Curie constant $C=3.35 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, and a Weiss constant $\theta=-3.87 \text{ K}$ (Fig. 6b, Inset). We apply the following expressions (Eq.2 and 3) for a 1D Co(II) chain to fit the data^[26]:

$$\chi_M = \frac{\chi_{\text{chain}}}{1 - \frac{2zj'\chi_{\text{chain}}}{Ng^2\beta^2}} \quad (2)$$

$$\chi_{\text{chain}} = \left(\frac{Ng^2\beta^2}{kT} \right) (2.0 + 0.0194x + 0.777x^2)(3.0 + 4.436x + 3.232x^2 + 5.834x^3)^{-1} \quad (3)$$

where $x=|J|/kT$; zj' represents the interaction between Co(II) ions and J is the parameter of exchange interaction between the neighboring Co(II) ions. The susceptibility values above 50 K were calculated, resulting in $J=-0.11 \text{ cm}^{-1}$, $g=1.85$, and the agreement factor defined by $R = \sum (\chi_M T_{\text{exp}} - \chi_M T_{\text{cal}})^2 / \sum (\chi_M T_{\text{exp}})^2$ was 7.2×10^{-5} . A negative J confirms a weak antiferromagnetic exchange that agrees with a negative θ value.

3 Conclusions

In summary, we have successfully constructed two new isomorphous coordination polymers from the 1,1'-(1,4-phenylenebis(methylene))bis-(1*H*-pyrazole-3,5-

dicarboxylic acid)) ligand under a similar synthetic procedure. The framework features anionic having a -2 charge and protonated dimethylamine cation by hydrolysis of DMF to maintain the electroneutrality of the complex. Magnetic studies indicate the presence of antiferromagnetic exchange for complexes **1** and **2**.

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