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1D Helical or Ladder Mn(II) Supramolecular Isomerism Based on Imidazo-[4,5-f]-1,10-Phenanthroline Ligand[1]

Y. Ren*, M. An, M. Zhang, J. Wang, L. Gao, and F. Fu

College of Chemistry and Chemical Engineering, Shaanxi Key Laboratory of Chemical Reaction Engineering,
Yan'an University, Yan'an, 716000 P.R. China
**e-mail: renyixia1@163.com*

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Abstract—Two isomeric Mn(II) complexes, $[Mn(IDP)SO_4 \cdot 2H_2O]_n$ (**I**) and $\{[Mn(IDP)SO_4 \cdot H_2O] \cdot H_2O\}_n$ (**II**), have been prepared by solvo-thermal reactions of imidazo-[4,5-f]-1,10-phenanthroline (IDP) ligand with manganese sulfate. The crystal structures of IDP, complexes **I** and **II** are characterized by single-crystal X-ray diffusion analyses (CIF files CCDC nos. 988128 (IDP), 988129 (**I**), and 988130 (**II**)). The structural analyses show that there are H-bonds and π–π stacking interactions resulting in the 3D supramolecular structure for IDP. Complex **I** exhibits 1D chain-like structure featuring the left- and right-handed helical chains, while in **II**, the 1D structure is a ladder-like structure. The π–π stacking interactions take an important role in the formation of supramolecule structures for complexes HL, **I**, **II** due to the large conjugated system of IDP ligand. The IR and UV-Vis absorption spectra of complexes **I** and **II** exhibit the difference, but the liquid-state photoluminescence of **I** and **II** is similar attributing to the intraligand π–π* transition.

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INTRODUCTION

The structural uncertainty of metal-organic coordination polymers increases the construction challenge of crystal engineering due to many factors such as metal coordination polyhedron, organic ligands, counter anions, solvent, and experimental conditions [1–3]. Supramolecular isomerism is a common phenomenon in the construction of coordination polymers, and it can be divided into two situations: (a) the metal centre ions are different but the structure is similar; (b) the base chemical compositions are the same but the networks are different [4–7]. Lots of supramolecular isomerism have been researched and reported not only for their structural diversity, but for the differences of their potential properties [8–11]. The induced reasons for the formation of the supramolecular isomerism are complex and the mechanism is still vague, in which the guest-induced, solvent-induced and reaction temperature-induced supra-molecular isomerisms are general [12–14], however, the additive-induced ones are several examples [15].

In this paper, we selected imidazo-[4,5-f]-1,10-phenanthroline (IDP) with the big conjugated system as an organic ligand to construct coordination polymers with Mn(II) salts in solvothermal conditions, and obtained a pair of supramolecular isomerisms with different structures – $[Mn(IDP)SO_4 \cdot 2H_2O]_n$ (**I**) and $\{[Mn(IDP)SO_4 \cdot H_2O] \cdot H_2O\}_n$ (**II**). Experiment analysis discovered that it was induced by an additive carboxyl organic ligand. Their crystal structures, IR, UV and FS spectrum have been determined and discussed.

EXPERIMENTAL

Materials and methods. All chemicals were commercially available and used as received without further purification. Elemental analyses (CHN) were performed using an Vario EL elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range of 4000–400 cm^{-1} on a Nicolet Avatar 360 FT-IR spectrometer. UV-Vis absorption experiments were performed on a SHIMADZU UV 2500PC spectrometer equipped with an integrating sphere for diffuse-reflectance spectroscopy, and the spectra were collected in the 200–800 nm range at room temperature. Fluorescence measurements were carried out with a F-4500 spectrofluorophotometer.

Recrystallization of IDP. The ligand was purchased commercially and recrystallized in water by hydrothermal method at 180°C for 72 h. The yellow prism-like crystals of IDP were collected by filtration, washed with ethanol and dried in air.

For $C_{13}H_8N_4$

anal. calcd., %:	C, 70.90;	H, 3.66;	N, 25.44.
Found, %:	C, 71.12;	H, 3.78;	N, 25.62.

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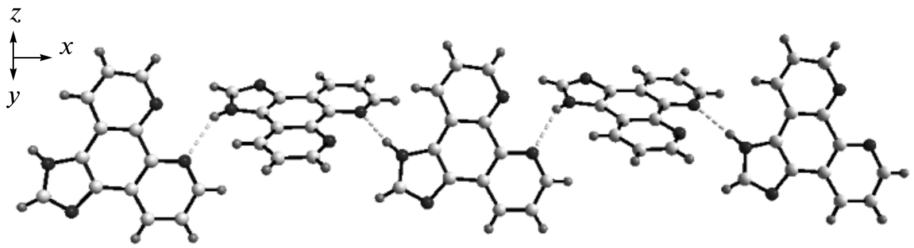

Fig. 1. 1D H-bonds chain along *x* axis of compound IDP.

IR data for IDP (KBr; ν, cm^{-1}): 3447 m, 3103 w, 2363 m, 2344 m, 1606 m, 1566 m, 1409 w, 1064 m, 932 m, 802 m, 738 m.

Synthesis of I. A mixture of $MnSO_4 \cdot H_2O$ (0.018 g, 0.1 mmol) and IDP (0.032 g, 0.1 mmol) in the mixed solvent of 1 mL H_2O and 1 mL isopropanol was stirred for 15 min, then added Na_2Hstp (0.013 g, 0.1 mmol), and placed in a 23-mL Teflon-lined autoclave and heated at 140°C for 96 h. The autoclave was cooled over a period of 10 h by natural cooling. The straw yellow lath-like crystals of **I** were collected by filtration, washed with ethanol, and dried in air (the yield was 10 mg, ~21% based on Mn).

For $C_{13}H_{12}N_4O_6SMn$

anal. calcd., %:	C, 38.34;	H, 2.97;	N, 13.76.
Found, %:	C, 38.65;	H, 2.88;	N, 13.54.

IR data for **I** (KBr; ν, cm^{-1}): 3445 m, 3103 w, 2365 m, 2337 m, 1607 m, 1559 m, 1419 w, 1117 m, 1067 m, 971 w, 940 m, 803 m, 731 m.

Synthesis of II. A mixture of $MnSO_4 \cdot H_2O$ (0.018 g, 0.1 mmol) and IDP (0.032 g, 0.1 mmol) in the mixed solvent of 1 mL H_2O and 1 mL ethanol was stirred for 15 min, then placed in a 23-mL Teflon-lined autoclave and heated at 140°C for 96 h. The autoclave was cooled over a period of 10 h by natural cooling. The straw yellow lath-like crystals of **II** were collected by filtration, washed with ethanol, and dried in air (the yield was 10 mg, ~21% based on Mn).

For $C_{13}H_{12}N_4O_6SMn$

anal. calcd., %:	C, 38.34;	H, 2.97;	N, 13.76.
Found, %:	C, 38.59;	H, 2.65;	N, 13.66.

IR data for **II** (KBr; ν, cm^{-1}): 3442 m, 3103 w, 2364 m, 2343 m, 1608 m, 1559 m, 1421 w, 1130 m, 1084 m, 1069 m, 988 w, 971w, 941 m, 809 m, 734 m.

X-ray structure determination. Single crystal X-ray diffraction analysis of compounds IDP, **I**, **II** were carried out on a Bruker SMART APEX CCD diffractometer equipped with a graphite monochromated MoK_α radiation (λ = 0.71073 Å). Raw data were integrated with the SAINT program [16]. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [17]. An empirical absorption correction was applied with the program SADABS [18]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were set in calculated positions and refined by a riding mode. The crystallographic details of compounds IDP, **I**, **II** are provided in Table 1, and the selected bond distances and angles are listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 988128 (IDP), 988129 (**I**), and 988130 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

In IDP ligand, the hydrogen bonds of N–H···N join the IDP molecules into one-dimension chains along *x* axis as shown in Fig. 1 (in N(3)–H(3A)···N(1), N···N 3.007 Å). The dihedral angel between two adjacent IDP molecules is 49.41°, which results the 1D chain into an undulating chain. Such 1D chains come into being 2D layer-structure in *xy* plane by π–π packing interactions (the distance of two adjacent IDP molecules is 3.578 Å) between IDP molecules with the big π-conjugated system (Fig. 2). Furthermore, these 2D layers stack into 3D supramolecular structure in ···ABAB··· order along *z* axis.

Single-crystal X-ray diffusion analysis indicates that compound **I** exhibits a one-dimensional double-helical chain-like structure. As shown in Fig. 3a, the Mn(1) ion is hexa-coordinated by two nitrogen atoms (N(1) and N(2)) from IDP ligand, two oxygen atoms (O(3) and O(4A)) from two SO_4^{2-} anions, and two oxygen atoms (O(1) and O(2)) from two coordinated water molecules. The center metal Mn(1) ion lies in a distorted slightly octahedral geometry, for which O(1) and O(4*A*) atoms are two vertexes and N(1), N(2), O(2), and O(3) consist of the equatorial plane of octahedron as shown in Fig. 3a. The Mn–N bond lengths are 2.253(1) and 2.277(2) Å, and Mn–O bonds range from 2.143(1) to 2.202(1) Å. The adjacent metal ions bridged by μ_2-fashion SO_4^{2-} anions into 1D chain-like structure and the IDP ligands hang vertically on the sides of the chain (Fig. 4). These chains are left- and

Table 1. Crystal data and structure refinement for compounds IDC, **I**, **II**

Parameter	Value		
	IDP	**I**	**II**
M	220.23	407.27	407.27
T, K	295(2)	296(2)	296(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$Pbca$	$P2_1/c$	$P2_1/c$
a, Å	14.570(4)	10.935(2)	10.1690(10)
b, Å	7.872(2)	7.0319(14)	6.5816(6)
c, Å	16.980(4)	19.761(4)	11.7392(11)
β, deg	90	99.459(2)	112.654(10)
V, Å^3	1947.5(9)	1498.8(5)	725.07(12)
Z	8	4	2
ρ_{calcd}, g cm^{-1}	1.502	1.805	1.870
μ, mm^{-1}	0.096	1.063	1.099
θ Range, deg	2.40–27.57	2.58–28.35	1.88–28.30
Reflection collected/unique	10572/2239	8926/3644	4521/1908
Reflections with $I > 2\sigma(I)$	1282	3232	1465
R_{int}	0.0645	0.0197	0.0257
Parameters refined	154	240	162
GOOF	1.021	1.034	1.049
R_1 $(I > 2\sigma(I))$*	0.0472	0.0284	0.0381
wR_2 (all data)	0.1097	0.0741	0.0870
Largest diff. peak/hole, e Å^{-3}	0.270/–0.207	0.495/–0.362	0.423/–0.640

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths for compounds IDP, **I** and **II***

Bond	d, Å	Bond	d, Å	Bond	d, Å
IDP		**I**		**II**	
C(1)–N(1)	1.325(3)	Mn(1)–O(4)$^{\#1}$	2.1429(1)	Mn(1)–O(7)$^{\#2}$	2.139(2)
C(5)–N(2)	1.387(2)	Mn(1)–O(3)	2.1613(1)	Mn(1)–O(7)$^{\#3}$	2.139(2)
C(6)–N(2)	1.318(3)	Mn(1)–O(1)	2.1972(1)	Mn(1)–O(6)	2.148(3)
C(6)–N(3)	1.357(3)	Mn(1)–O(2)	2.2017(14)	Mn(1)–O(9)	2.230(4)
C(7)–N(3)	1.375(2)	Mn(1)–N(1)	2.2531(1)	Mn(1)–N(3)	2.275(3)
C(11)–N(4)	1.324(2)	Mn(1)–N(2)	2.2768(1)	Mn(1)–N(4)	2.295(3)

* Symmetry codes: $^{\#1}$ $1 - x, 0.5 + y, 0.5 - z$; $^{\#2}$ $1 - x, -y, 1 - z$; $^{\#3}$ $1 - x, 0.5 + y, 1 - z$.

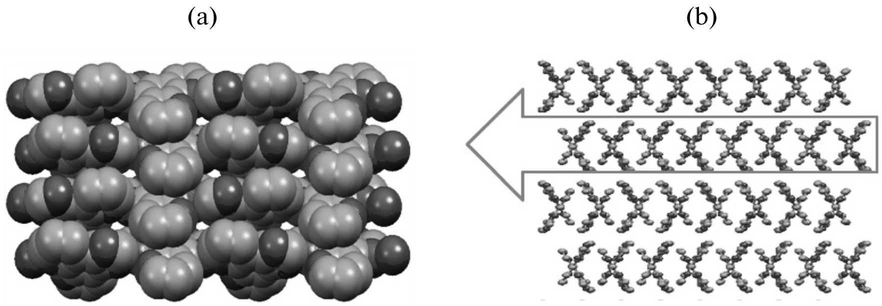

Fig. 2. 2D layer-like structure by π–π packing interactions base on 1D H-bonds chains (a) and 3D supramolecular structure base on 2D layer in ···ABAB··· order along *z* axis (b) in compound IDP.

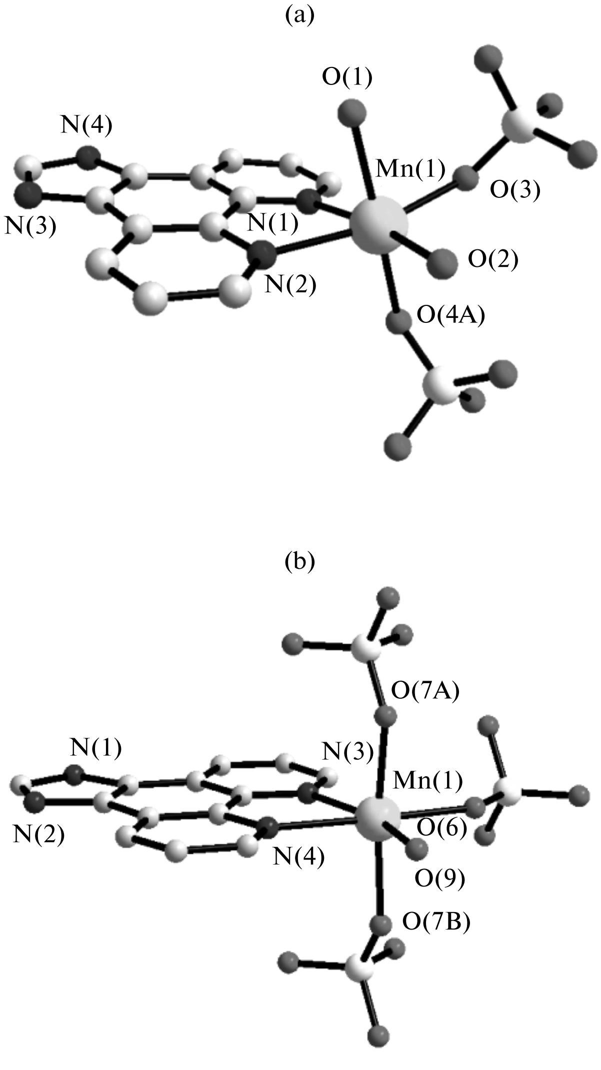

Fig. 3. Coordination environment of Mn(1) in compounds **I** (a) and **II** (b). All H atoms are deleted for clarity. Symmetry codes: 1 – *x*, 0.5 + *y*, 0.5 – *z* (**I**); (*A*) 1 – *x*, 0.5 + *y*, 1 – *z*; (*B*) 1 – *x*, –*y*, 1 – *z* (**II**).

right-handed helical chains based on the metal ions and SO_4^{2-} anions, and the IDP ligands from two adjacent chains fasten each other in slide fastener mode by π–π packing interactions (3.201 and 3.271 Å) into 2D layer-like supramolecule structures.

Compound **II** displays one-dimensional ladder-like chain structure. There are one Mn(II) atom, one IDP ligand, one SO_4^{2-} anion, one coordination water molecule and one lattice water molecule in the asymmetric unit of **II**. The center manganese(II) atom adopts slightly octahedral coordination geometry, surrounded by two nitrogen atoms (N(3) and N(4)) of IDP ligand, three oxygen atoms (O(6), O(7) and O(7A)) from three SO_4^{2-} anions and one oxygen atom (O(9)) from one coordination water molecule (Fig. 3b). Each IDP ligand acts as a chelated mode to coordinate to one manganese(II) atom by its N(3) and N(4) atoms. The Mn–N bond lengths are 2.275(3) and 2.295(3) Å, and Mn–O bonds range from 2.139(2) to 2.230(4) Å. Differed from compound **I**, the adjacent Mn^{2+} ions are linked by μ_3-fashion SO_4^{2-} anions into 1D ladder-like chain with the hanging IDP ligands on its two sides. The protrudent IDP molecules play an important role in structure construction as interlinkages by π–π stacking interactions (the face-to-face distance is 3.291 Å) (Fig. 5).

The IR spectrum of compounds IDP, **I**, **II** exhibits the stretching vibration of ν_{-N-H} of IDP ligand at 3442–3447 cm^{-1}. For these compounds, the skeleton vibration of the phenyl ring appear at 3103, 1606–1608 and 1566–1559 cm^{-1}. Furthermore, the IR spectrum of the bidentate bridging and tridentate coordinated SO_4^{2-} anions in compounds **I** and **II** are different. In **I**, the peak at 1117 cm^{-1} can be attributed to the ν(S–O) of the bidentate bridging coordinated SO_4^{2-} anions, while there are two bands at 1130 and 1084 cm^{-1} assigning to the tridentate coordinated ones. The symmetry decreasing of SO_4^{2-} anions results into the abruption of absorption bonds of SO_4^{2-} anions [19].

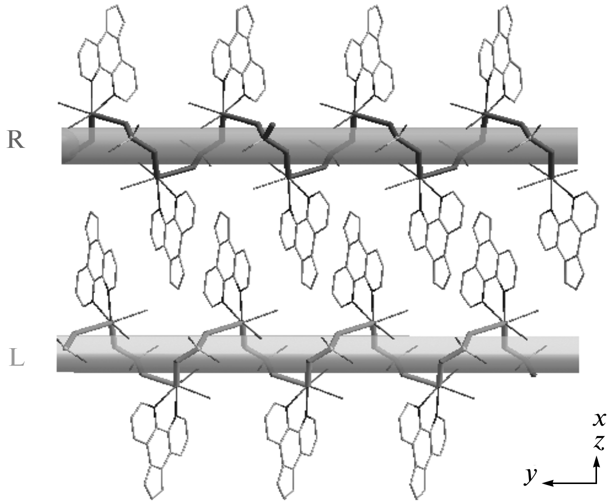

Fig. 4. Double helical chains in compound **I**.

The analysis of IR spectrum of the complex is in agreement with its crystal structure and charge balance consideration.

The UV-Vis absorption spectra for compounds **I** and **II** were recorded in reflectance mode in DMF solution at room temperature. According to the spectra, the wavelength absorption bands of **I** occur at 260 and 284 nm. The absorption bands of **II** (258 and 288 nm) are similar to those of **I**, except that the intensity of the peaks are different. The sharp absorption bands at 260 and 258 nm for **I** and **II** can be assigned to *n*–π transitions of S=O of SO_4^{2-} anions [20, 21], and the intensity of **I** is stronger than that of **II**. The bands at 284 and 288 nm are corresponding to π–π transitions of the IDP ligand.

Photoluminescence spectra of compounds IDP, **I**, **II** have been measured under similar conditions. In the spectra, compound **I** displays an intense emission light with a maximum at ~423 nm, slightly red-shift compared with that of the IDP ligand (419 nm), which can be attributed to π–π* transition of intra-ligand. The maximum emission band of **II** occurs at 417 nm also due to the emission of ligand [22].

Thus, we have successfully prepared two manganese(II) supramolecular isomerisms with similar chemical composition, but different structures for the role of one water molecule. This might be attributed to the carboxyl-induced solvo-thermal synthesis. Structural analyses indicate that compound **I** is 1D double-helix structure with two coordinated water molecules, while compound **II** is 1D ladder-like structure with one coordinated and one lattice water molecules.

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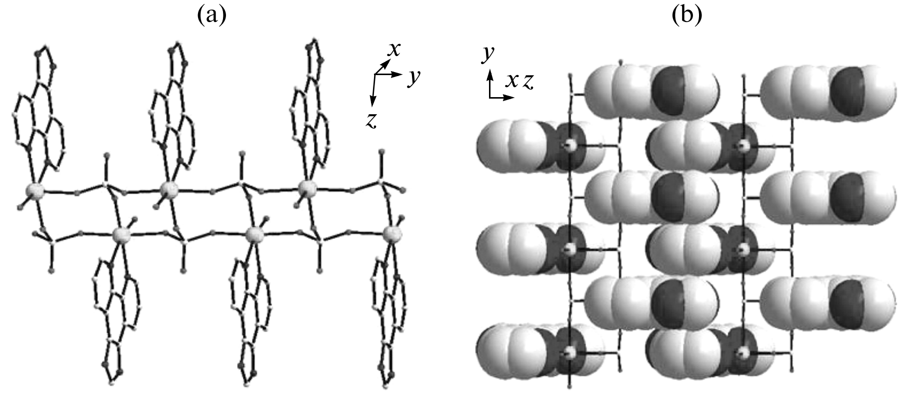

Fig. 5. 1D ladder-like chains (a) and 2D layer by π–π packing interactions (b) in compound **II**.

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