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Hydrothermal Synthesis, Crystal Structure, and Photoluminescence of Pb(II) and Mn(II) Coordination Polymers Based on Imidazo[4,5-f][1,10]phenanthroline[1]

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Abstract—Two new coordination polymers, $[Pb(IDPT)_2(NO_3)_2]$ (**I**) and $[Mn(IDPT)(SO_4)(H_2O)_2]$ (**II**) (IDPT = imidazo[4,5-f][1,10]phenanthroline), were synthesized by hydrothermal method and characterized by elemental analysis and single-crystal X-ray diffraction technique. The results reveal that the complex **I** belongs to monoclinic crystal system, space group $C2/c$ and complex **II** belongs to monoclinic crystal system, $P2_1/c$ space group. The cell parameters are: a = 19.1970(13), b = 7.3875(5), c = 17.3825(12) Å, β = 100.47(10)°, V = 2424.0(3) Å^3, Z = 4, F(000) = 1488 for **I**; a = 10.9135(6), b = 7.0230(4), c = 19.7034(10) Å, β = 99.32(10)°, V = 1490.25(14) Å^3, Z = 4, F(000) = 828 for **II**. In the structure of complex **I**, the metal center Pb(II) is six-coordinated, displays an octahedral geometry. Each molecule is further connected with neighboring one via π–π interactions into 1D chain. In complex **II**, Mn(II) is six-coordinated to form a distorted octahedral geometry. Compound **II** displays 1D supramolecular chain formed through hydrogen bonds. Additionally, the fluorescent properties for the complexes were investigated. Complexes **I** and **II** exhibit strong photoluminescence with emission maximum at 583 and 529 nm at room temperature.

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INTRODUCTION

The design and synthesis of coordination polymers have been increasing over the past decade owing to their diverse topologies and potential applications in the area of magnetism, porosity and luminescence [1–7]. At present, many metal-organic complexes with novel structure and good properties were successfully prepared through molecular self-assembly [8]. The critical issue is the rational choice of metal ions and organic ligands during the self-assembly process. Usually, the complexes were prepared through the assembly of transition metal ions with nitrogen-containing ligands, such as phenanthroline, imidazole and pyridine. We choose the imidazo[4,5-f][1,10]phenanthroline (IDPT) as the major ligand to design and synthesized new coordination polymers. Two new complexes were obtained and they were characterized by elemental analysis and single crystal X-ray diffraction method. And the properties of fluorescence were also investigated.

EXPERIMENTAL

Materials and instruments. All reagents and solvents for the synthesis and analysis were commercially available and used as received. Elemental analysis was performed on a PerkinElmer 240 C element analyzer. Crystal structure was collected on Bruker SMART APEX II CCD single crystal diffractometer. Solid-state uorescence spectra were recorded at room temperature with an F-4500 equipped with a xenon lamp and a quartz carrier.

Synthesis of $[Pb(IDPT)_2(NO_3)_2]$ (I). A mixture of $Pb(NO_3)_2$ (132 mg, 0.4 mmol), IDPT (88 mg, 0.4 mmol), 2,5-dimercapto-1,3,4-thiadiazole (DMTD) (60 mg, 0.4 mmol), NaOH (16 mg, 0.4 mmol), and distilled water (10 mL) was sealed in a 25 mL teflon-lined stainless steel vessel and heated to 150°C for 48 h. After cooling to room temperature in 24 h, the products were orange crystals that were washed with distilled water to give pure samples (the yield was 30% based on Pb(II)).

For $C_{26}H_{16}N_{10}O_6Pb$

anal. calcd., %:	C, 40.43;	H, 2.07;	N, 18.14.
Found, %:	C, 40.03;	H, 1.93;	N, 17.58.

Synthesis of $[Mn(IDPT)(SO_4)(H_2O)_2]$ (II). A mixture of $MnCl_2 \cdot 6H_2O$ (39.6 mg, 0.2 mmol), IDPT (88 mg, 0.4 mmol), DMTD (60 mg, 0.4 mmol), NaOH (16 mg, 0.4 mmol), and distilled water (10 mL)

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was sealed in a 25 mL teflon-lined stainless steel vessel and heated to 150°C for 48 h. After cooling to room temperature in 24 h, the orange crystals were obtained (the yield was 36% based on Mn(II)).

For $C_{13}H_{12}N_4O_6SMn$
anal. calcd., %: C, 38.30; H, 2.95; N, 13.75.
Found, %: C, 37.89; H, 2.66; N, 13.04.

X-ray structure determination. Diffraction intensity data of single crystals of the complex was collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatic MoK_α radiation ($\lambda = 0.71073$ Å) by using a ω-scan mode. An empirical absorption correction was applied using the SADABS programs [9]. The structures was solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHEXL-97 [10, 11]. All non-hydrogen atoms were refined by Fourier syntheses. The hydrogen atoms bonded to carbon were located by geometrical calculations and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data, experimental details and structural analyses of the metal complexes was summarized in Table 1. Selected bond and angle parameters are listed in Table 2. Hydrogen bonds of complex **II** are listed in Table 3.

Crystallographic data for two complexes have been deposited with the Cambridge Crystallographic Data Centre (nos. 834627 (**I**) and 814229 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Two new coordination polymers **I** and **II** were obtained when we used IDPT and DMTD as mixed ligands to react with Pb^{2+} or Mn^{2+} cations under hydrothermal conditions. From the results of single crystal X-ray diffraction analysis we can know that the DMTD ligand was not involved in complex **I** and in complex **II** sulfate anion was found to coordinate to the Mn^{2+} cation. This might be attributed to the DMTD decomposing into sulfate anion with the catalysis of manganese ions.

The fundamental unit for complex **I** is shown in Fig. 1. Each Pb^{2+} ion is coordinated by four N-atoms from two same IDPT ligands and two oxygen atoms from two same nitrates in a distorted octahedral coordination geometry. The bond lengths Pb(1)–N range from 2.535(3) to 2.607(3) Å, and the bond lengths for Pb(1)–O is 2.875(3) Å. The bond angles between the donor atoms around the Pb(II) center range from 64.16(9)° to 144.10(9)°. In the crystal structure, the centroid distances between eighboring parallel IDPT ligands of the neighboring chains are 3.4683, 3.5159, and 3.6522 Å, which reveals that there exist π–π stacking interactions between adjacent IDPT ligands. Hence,

Table 1. Crystallographic data and structure refinement summary for **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	771.68	407.27
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
Unit cell dimensions:		
a, Å	19.1970(13)	10.9135(6)
b, Å	7.3875(5)	7.0230(4)
c, Å	17.3825(12)	19.7034(10)
β, deg	100.47(10)	99.32(10)
V, Å^3	2424.0(3)	1490.25(14)
Z	4	4
ρ_{calcd}, mg m^{-3}	2.114	1.815
F(000)	1488	828
θ range, deg	2.16–25.00	1.89–24.99
Reflections collected/unique	6022/2138	7346/2614
R_{int}	0.0248	0.0200
Reflections with $I > 2\sigma(I)$	2032	2334
Data/restraints/parameters	2138/18/227	2614/0/226
Goodness-of-fit on F^2	1.061	0.98
R_1, wR_2 ($I > 2\sigma(I)$)	0.0189, 0.0503	0.0274, 0.0732
R_1, wR_2 (all data)	0.0206, 0.0512	0.0315, 0.0750
Largest diff. peak and hole, e/Å^3	0.746 and –0.555	0.509 and –0.243

Table 2. Selected bond lengths and bond angles for **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
Pb(1)–N(1)	2.535(3)	Pb(1)–O(1)	2.875(3)
Pb(1)–N(2)	2.607(3)		
		II	
Mn(1)–O(1)$^{\#2}$	2.1394(16)	Mn(1)–O(1*w*)	2.1924(15)
Mn(1)–O(2)	2.1590(15)	Mn(1)–N(1)	2.2519(17)
Mn(1)–O(2*w*)	2.1923(16)	Mn(1)–N(2)	2.2739(18)
Angle	ω, deg	Angle	ω, deg
		I	
N(1)$^{\#1}$Pb(1)N(1)	90.09(13)	N(1)$^{\#1}$Pb(1)O(1)	144.10(9)
N(1)$^{\#1}$Pb(1)N(2)	84.13(9)	N(1)Pb(1)O(1)	70.46(9)
N(1)Pb(1)N(2)	64.16(9)	N(2)$^{\#1}$Pb(1)O(1)	83.54(9)
N(2)$^{\#1}$Pb(1)N(2)	135.23(13)	N(2)Pb(1)O(1)	111.65(9)
		II	
O(1)$^{\#2}$Mn(1)O2	91.52(6)	O(1)$^{\#2}$Mn(1)N(1)	88.71(6)
O(1)$^{\#2}$Mn(1)O(2*w*)	174.65(6)	O(2)Mn(1)N(1)	93.70(6)
O(2)Mn(1)O(2*w*)	86.82(6	O(2*w*)Mn(1)N(1)	86.33(7)
O(1)$^{\#2}$Mn(1)O(1*w*)	91.53(6)	O(1*w*)Mn(1)N(1)	168.63(6)
O(2)Mn(1)O(1*w*)	97.65(6)	O(1)$^{\#2}$Mn(1)N(2)	96.27(6)
O(2*w*)Mn(1)O(1*w*)	93.73(6)	O(2)Mn(1)N(2)	164.70(6)

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x + 1, y, -z + 1/2$; $^{\#2}$ $-x + 2, y - 1/2, -z + 1/2$.

Table 3. Geometric parameters of hydrogen bonds for **II***

Contact D–H···A	Distance, Å			Angle DHA, deg
	D···H	H···A	D···A	
N(3)–H(3A)···O(4)$^{\#3}$	0.86	1.92	2.766(2)	167
O(1*w*)–H(12*w*)···O(2)$^{\#2}$	0.84	2.11	2.945(2)	174
O(1*w*)–H(11*w*)···O(3)$^{\#1}$	0.84	1.90	2.713(2)	160
O(2*w*)–H(21*w*)···N(4)$^{\#4}$	0.85	1.91	2.742(2)	168
O(2*w*)–H(22*w*)···O(3)	0.85	1.99	2.739(2)	147

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x + 2, y - 1/2, -z + 1/2$; $^{\#2}$ $-x + 2, y + 1/2, -z + 1/2$; $^{\#3}$ $-x + 1, y - 1/2, -z + 1/2$; $^{\#4}$ $-x + 1, -y + 2, -z$.

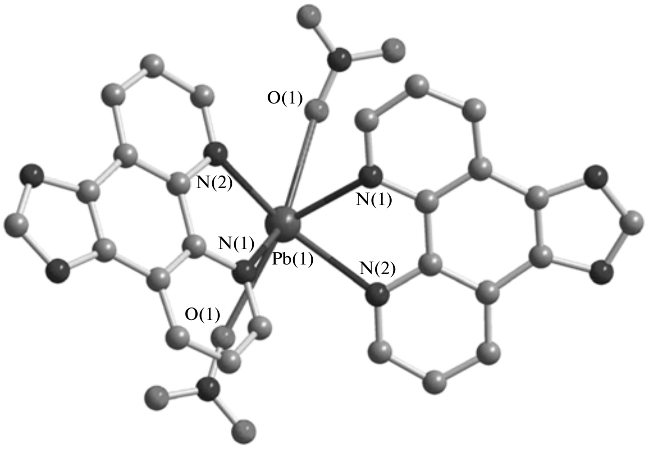

Fig. 1. Molecular structure of complex **I**. Hydrogen atoms have been omitted for clarity.

the 1D supramolecular chain of complex **I** was formed via π–π stacking interactions, as shown in Fig. 2.

In compound **II**, each independent Mn^{2+} cation is coordinated by two N atoms of IDPT ligands and four O atoms from two sulfate anions and two water molecules to furnish a distorted octahedral geometry, as shown in Fig. 3. The bond lengths Mn(1)–N(1) and Mn(1)–N(2) are 2.2519(17) and 2.2739(18) Å. The bond lengths of Mn(1)–O(1), Mn(1)–O(2), Mn(1)–O(1*w*), Mn(1)–O(2*w*) are very close (2.1394(16), 2.11590(15), 2.1924(15), and 2.1923(16) Å, respectively). There are strong hydrogen bonds in complex **II** as shown in Table 3. The distances of D···A range from 2.713(2) to 2.945(2) Å. The angles of the D···H···A range from 147° to 174°. So 1D supramolecular chain of complex **II** is formed via hydrogen bonds (Fig. 4).

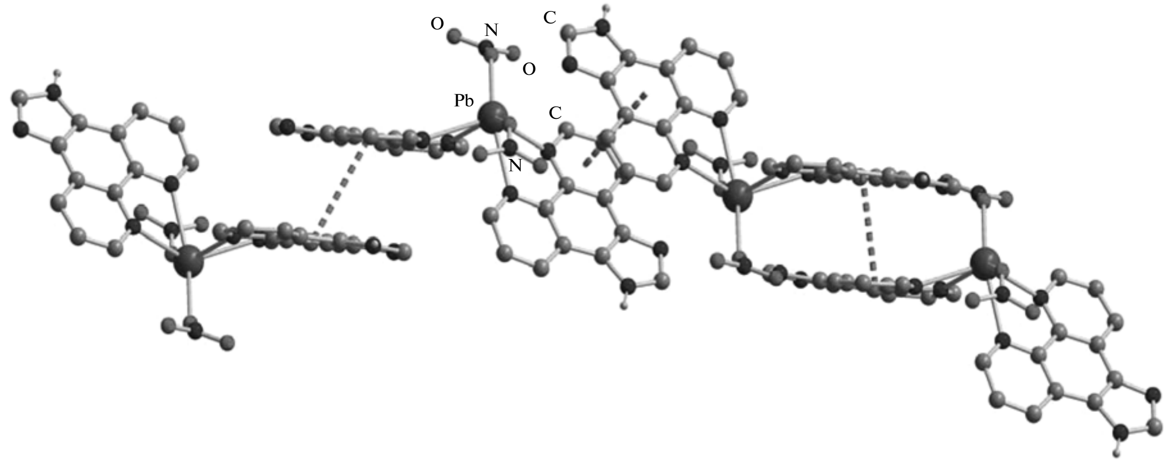

Fig. 2. The 1D supramolecular chain through π–π interactions for complex **I**.

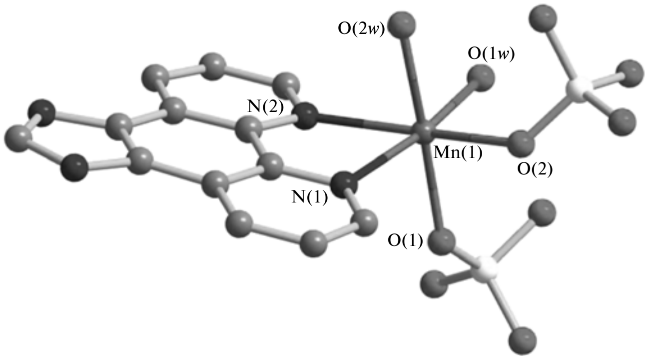

Fig. 3. Coordination environment of Mn(II) atom in complex **II**. Hydrogen atoms have been omitted for clarity.

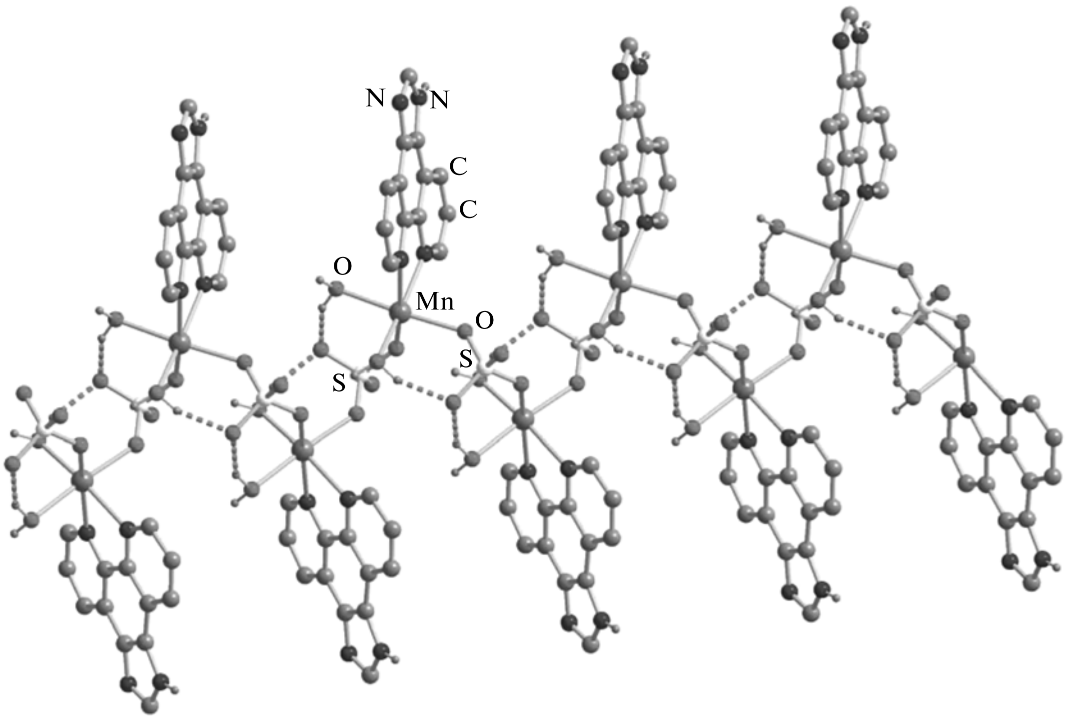

Fig. 4. 1D supramolecular chain formed through hydrogen bonds of complex **II**.

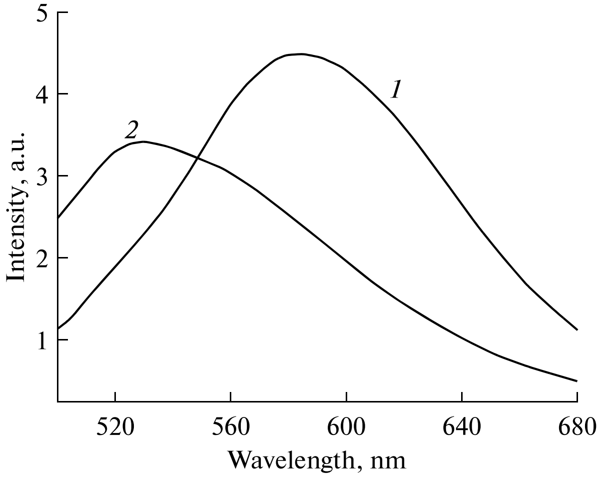

Fig. 5. Photoluminescent spectra of complexes **I** (*1*) and **II** (*2*) at room temperature.

Metal-organic coordination polymers with transition metal have been investigated for their photoluminescence [12]. The solid-state fluorescent spectrums of **I** and **II** at room temperature are depicted in Fig. 5. Complex **I** displays fluorescent emission maximum at ~583 nm upon an excitation at 369 nm. Complex **II** exhibits an intense photoluminescence with an emission at 529 nm on excitation at 369 nm. As we know, Mn^{2+} ion is difficult to oxidize or reduce, thus, the fluorescent emissions of complexes **I** and **II** are neither metal-to-ligand nor ligand-to-metal charge transfer, it may be attributable to $\pi-\pi^*$ transitons [13, 14].

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