One 1D metal-organic frameworks based on *N*-heterocyclic ligand and 5-Amino-isophthalic acid: synthesis, structure, and photoluminescent properties

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Abstract: One complex $[Mn(dnpt)(aic)]_n$ [dnpt = 2-(4-nitrophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline, aic = 5-Amino-isophthalic acid] was obtained from hydrothermal reaction and characterized by elemental analysis, IR, and single-crystal X-ray diffraction. The crystal structure shows that the manganese ion is coordinated with two nitrogen atoms of one dnpt molecule and four oxygen atoms from three aic molecules, forming a distorted octahedral coordination geometry. Each Mn(II) atom is linked by aic ligands with neighbor Mn(II) atoms, forming an infinite one-dimensional (1D) double-chain structure. The luminescent properties for the ligand and complex 1 are also discussed in detail. CCDC 1030059

Key words: hydrothermal synthesis; Mn(II) complex, crystal structure, fluorescence, 5-Amino-isophthalic acid

1 Introduction

The designed synthesis and characterization of metal-organic frameworks (MOFs) have achieved considerable progress in recent years. The increasing interest in this field is justified not only for their fascinating molecular structures, but also for their potential applications in catalysts, luminescent materials, gas storage, magnetic materials[1-3] and so on. Consequently, numerous new complexes have been produced mostly by using appropriate organic ligands, especially bridging ligands containing multi-dentate oxygen, nitrogen, or sulfur donors to coordinate with the transition metal centers[4-6]. Among poly-carboxylates, the best studied are dicarboxylates, tricarboxylates, and biphenyldicarboxylates. 2-(Pyridin-2-yl)pyridine, 4-(pyridin-4-yl)pyridine, and 1,10-phenanthroline can act as terminal ligands and provide supramolecular interaction sites for molecular recognition. Take 5-Amino-isophthalic acid (aic) ligand for example, this ligand can function in chelating bis-bidentate, bis-monodentate, mono-bidentate(syn–syn), bridging bis-bidentate, monodentate–bidentate or chelating/bridging bis-bidentate modes. Among the organic ligands, the chelate 1,10-phenanthroline (phen) and its derivatives have been extensively used in the preparation of many MOFs with versatile topologies. It is because their excellent coordinating capacities, hydrogen bond donors and acceptors, and potential supramolecular recognition sites for π-π stacking interactions. The polycyclic aromatic bidentate ligands, such as 2,2-bipyridine, 4,4-bipyridine and 1,10-phenanthroline, are frequently used corporately with polycarboxylates, leading to many novel architectures[7-9]. In order to obtain novel functional carboxyl complexs and investigate their structure-function relationship, we synthesized a new ligand 2-(3-chlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline (dnpt) (scheme 1), and then a novel 1D complex $[Mn(dnpt)(aic)]_n$ (**1**) was synthesized. In this paper, we research the synthesis, crystallography, and luminescent properties of complex (**1**).

2 Experimental

2.1 Reagents and instruments

With the exception of the ligand dnpt, all the other chemicals from commercial sources were of AR grade and used without further purification. Thermogravimetric analysis was performed using a Perkin-Elmer TG-7 analyzer at the rate of 10 ℃/min rise of temperature in nitrogen atmosphere. The FT-IR spectrum was recorded with KBr pellets on a Perkin-Elmer 240C spectrometer. Crystal structure determination was carried out on a Bruker SMART APEX II CCD X-ray diffractometer. Elemental analyses of C, H and N were performed on a PE-2400 elemental analyzer. Fluorescence spectra were recorded on a FLSP 920 Edinburgh fluorescence spectrometer.

2.2 Synthesis of the ligand (dnpt)

A mixture of 4- nitrobenzaldehyde (0.38 g, 2.5 mmol), 1,10-phenanthroline-5,6-dione (0.525 g, 2.5 mmol), ammonium acetate (3.88 g, 50 mmol) and glacial acetic acid were refluxed for 12 h, cooled the mixture to room temperature and added concentrated aqueous ammonia to neutralize, we collected a yellow precipitate and washed with water. The crude product dissolved in ethanol was purified by filtration on silica gel (60–100 mesh; ethanol), then the principal yellow band was collected. Yellow products were obtained by evaporation of the solution[10].

2.3 Syntheses and crystal growth

A mixture of A mixture of dnpt (0.10 g, 0.3 mmol), $MnSO_4.H_2O$ (0.051 g, 0.3 mmol), aic (1.000 g, 0.6 mmol) in H_2O (18ml) was stirred for 30 min in air, then transferred to a 25 mL

Telfon-lined stainless steel autoclave and heated to 160 ℃ for 3 d. After cooling to room temperature at a rate of 5 ℃·h^{-1}, yellow block crystals of **1** were obtained. The crystals were filtered, washed with distilled water and dried at ambient temperature to give a yield of about 81% yield based on Mn. $C_{26}H_{17}MnN_6O_6$: calcd. C 54.36, H 4.74, N 14.63%; found: C 54.38, H 4.71, N 14.59%. IR (KBr, cm^{-1}): 3435(s), 1611(s), 1546(vs), 1339(vs), 1225(s), 1078(s), 751(s), 706(s).

2.4 X-ray structure determination

The diffraction data was collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated MoKa radiation (λ=0.71073 Å) at 293(2) K in the range of $1.56 \leq \theta \leq 25.18°$. All the structures were solved by direct methods using the program SHELXS-97[11] and refined by full-matrix least-squares techniques against F^2 using the SHELXTL-97 crystallographic software package[12]. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically, whereas the hydrogen atoms of the organic molecules were placed by geometrical considerations and were added to the structure factor calculation. The detailed crystallographic data and structure refinement parameters for the title complex are summarized in Table 1.

3 Results and discussion

3.1 Description of the structure

Single-crystal X-ray diffraction analysis reveals that complex 1 possesses a discrete one-dimensional structure that crystallizes in space group *C*2/*c*. The molecular structure of complex **1** is shown in Fig. 1, and the 1 D chain of the complex is displayed in Fig. 2. The 2D structure of complex **1** linked by N–H···O hydrogen bonds is suggested in Fig. 3. Selected bond distances and angles are presented in Table 2.

The asymmetric unit of **1** (show in Fig.1) consists of one Mn^{2+} ion, two dnpt free ligands, and two aic ligands. The central Mn^{2+} ion adopts slightly distorted octahedral geometry coordinated by two nitrogen atoms (N1, N2) from one dnpt ligand, and four O atoms (O1, O2, O3, O4) from three different aic^{2-} ligands. The bond distances of Mn–O in 1 are from 2.13 to 2.28 Å, and those of Mn–N bond distances fall in the 2.23 to 2.27 Å range. The O(N)-Mn-N(O) angles range are from 89.70 to 144.70°. The distances of Mn–O/N bond lengths are all consistent with corresponding bond lengths found in the literature[13-15].

The aic ligands adopt two different coordination modes: (1) one aic ligand coordinates to three Mn ions through four carboxylic oxygen atoms in mono-bridging and bidentate chelating fashion; (2) another aic ligand coordinates to three Mn ions through three carboxylic oxygen atoms in mono-bridging chelating fashion, which give rise to a 1D double-chain structure (Fig. 2). It should be mentioned that in the unit of **1**, two types of rings formed: 8-membered ring with the distance of Mn···Mn is 3.104 Å; The 16-membered ring with the distance of Mn···Mn is 7.650 Å.

The bond distances of C-C and C-N within the aromatic rings are normal. Moreover, there are two kinds of hydrogen bonds in the title complex: N-H···O, and C-H···O hydrogen bonds. Hydrogen bonding interactions are usually important in the synthesis of supramolecular architectures.

3.2 Photoluminescent properties

The PL spectrum of title complex was investigated in the solid state at room temperature. As indicated in Fig. 3, the emission peaks are 556 upon excitation at 325nm. In order to understand the nature of these emission bands, the PL properties of free ligand dnpt were analyzed, showing it exhibits the strongest emission peaks at about 447 nm (excitation at 325 nm) from 300 to 800 nm. Compared with the PL spectrum of free ligand, the red shifts for **1** may be due to the chelating and bridging effects of the relevant ligands to the metal atoms. The emission bands for the free ligands are probably attributable to the π*-n transitions. However, the effect of the microenvironment between ligands and complex on the luminescence properties still needs further investigations.

3.3 UV–Vis Absorption Spectra

The UV–Vis absorption spectra of dnpt ligand and complex 1 are determined in the solid state at room temperature. The result suggests that complex 1 exhibits absorption bands at 412 nm (Fig. 4). The ligand dnpt shows two absorption bands at 232 and 274 nm. The absorption band of complex 1 is red-shifted by 138–180 nm relative to that of free ligand dnpt. After coordination, the formation of more large conjugated system may be the reason for the strong red-shift. The above analyses for UV–Vis spectral are in agreement with the determined crystal structure of complex 1.

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Table 1 Crystal data and structure refinement parameters for the title complex

Empirical formula	$C_{26}H_{17}MnN_6O_6$
Formula weight	564.40
Size/mm	0.285x0.178x0.146
$^{\theta}$range for date collection/(°)	1.56 -25.18
Crystal system	monoclinic
space group	*P*-1
a/Å	13.783(3)
b/Å	26.154(6)
c/Å	14.301(3)
β/(°)	111.249(4)
V/Å ^{3}	4804.7(1)
D/(g.cm^{-3})	1.552
Z	8
F(000)	2224
μ/mm	0.609
Reflections collected	13936
Independent reflections	4306
Final GOF	0.878
*R*1 ,*w*R2 [$I > 2\sigma(I)$]	0.1415, 0.2821
Largest diff. peak and hole/(e.Å^{-3})	3.487, -2.553

Table 2 Selected bond lengths [Å] and bond angles [°] for the title complex

bond	Dist.	bond	Dist.
Mn(1)-O(3)	2.138(10)	Mn(1)-O(2)	2.221(9)
Mn(1)-O(1)	2.281(9)	Mn(1)-O(4)	2.225(10)
Mn(1)-N(1)	2.236(9)	Mn(1)-N(2)	2.274(10)
Angle	(°)	Angle	(°)
O(3)-Mn(1)-O(2)	91.9(3)	O(3)-Mn(1)-O(4)	86.4(4)
O(2)-Mn(1)-O(4)	107.1(4)	O(3)-Mn(1)-O(1)	148.4(3)
O(2)-Mn(1)-O(1)	58.2(3)	O(4)-Mn(1)-O(1)	92.8(4)
O(3)-Mn(1)-N(1)	120.1(4)	O(2)-Mn(1)-N(1)	144.7(4)
N(1)-Mn(1)-O(4)	90.4(3)	N(1)-Mn(1)-O(1)	91.4(3)
O(3)-Mn(1)-N(2)	94.2(4)	O(2)-Mn(1)-N(2)	89.7(4)
O(4)-Mn(1)-N(2)	163.2(4)	O(1)-Mn(1)-N(2)	95.3(4)
N(1)-Mn(1)-N(2)	74.8(3)		

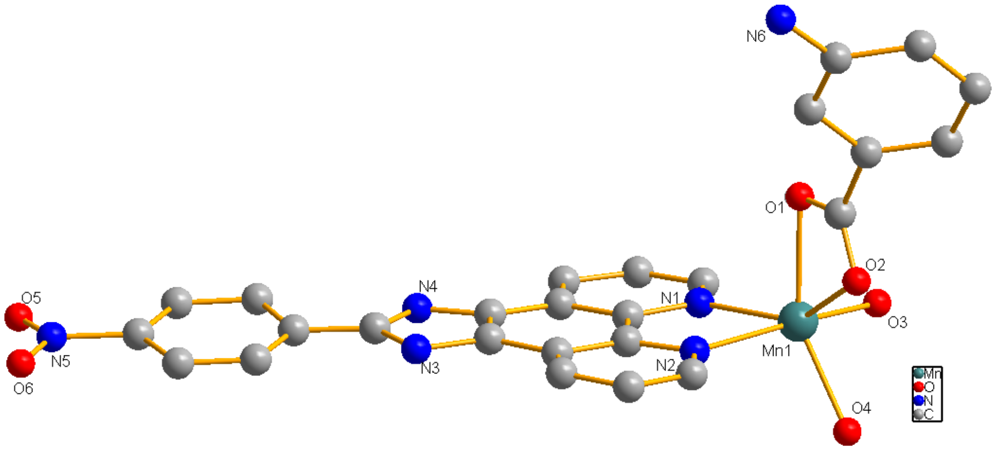


Fig.1 the molecular complex **1** (hydrogen atoms were omitted)

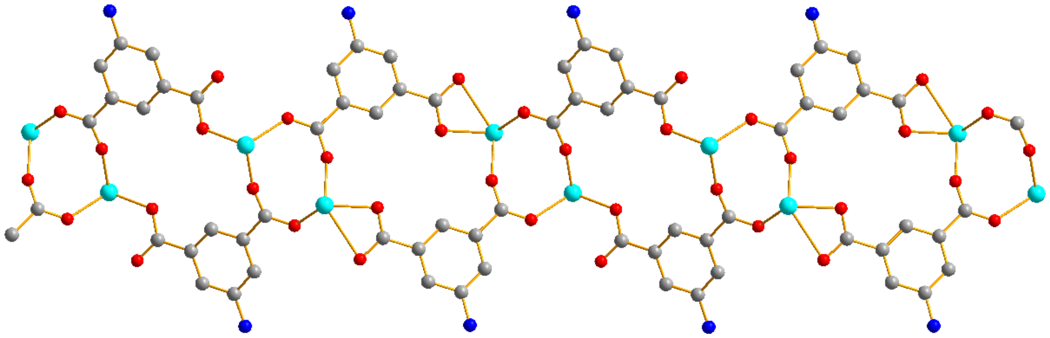


Fig.2 simplified 1D chain structure of complex **1** (hydrogen atoms and dnpt ligands were omitted)

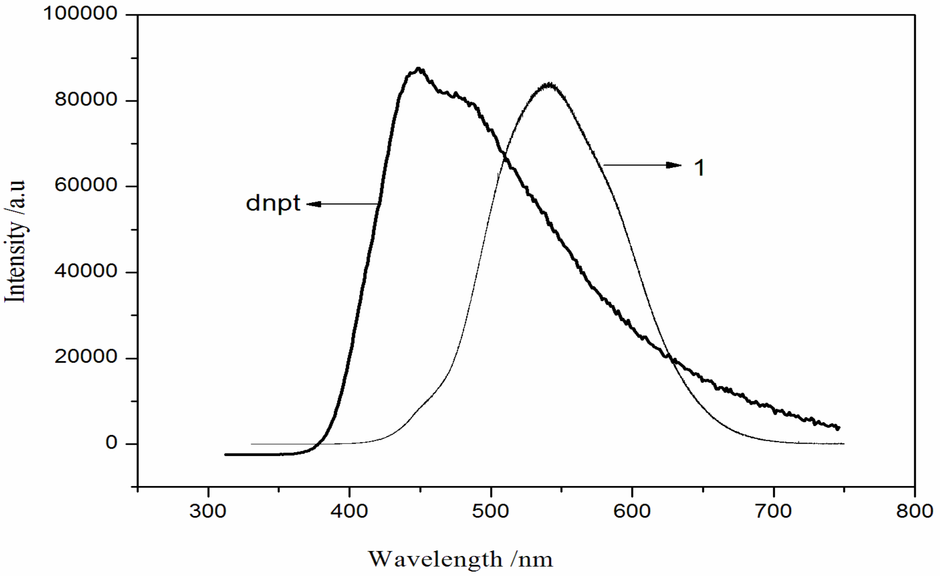


Fig.3 Luminescent spectrum of complex **1** and ligands in solid state at room temperature

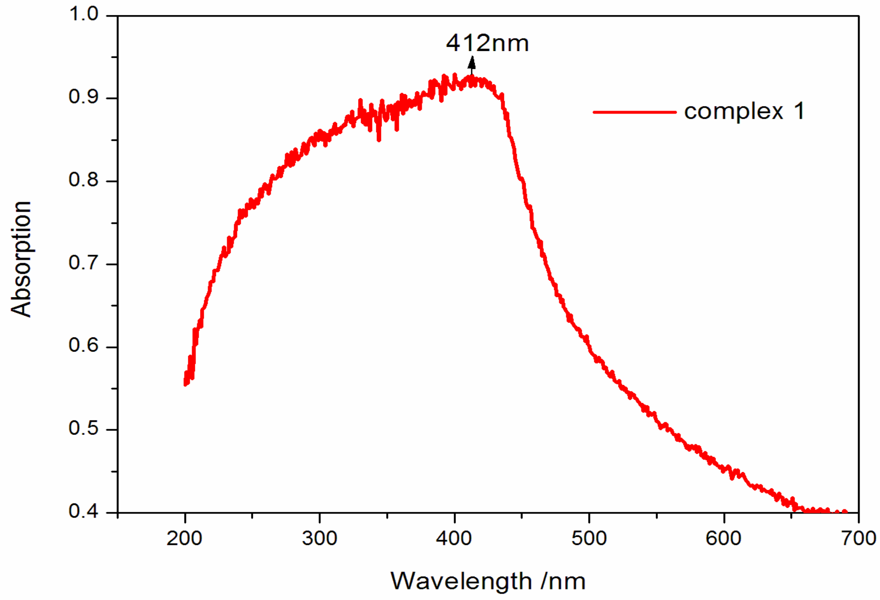
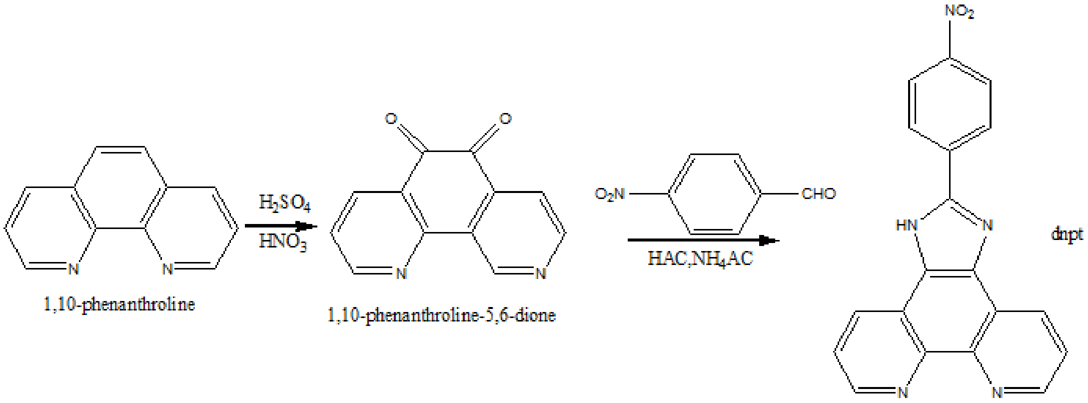


Fig.4 UV–Vis spectrum of complex **1** in solid state at room temperature



Scheme 1 the synthesis of dnpt