

Synthesis, Structure and Theoretical Calculation of Metal Coordination Polymers with Pyrazine-2,3-dicarboxylic Acid and 3-(2-Pyridyl)pyrazole as Co-ligands^①

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ABSTRACT A new 2D metal coordination polymer (MCP), [Mn(pzdc)_{0.5}(L)]_n (**1**, pzdc = pyrazine-2,3-dicarboxylic acid, HL = 3-(2-pyridyl)pyrazole), was synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction, powder XRD, FT-IR, TG, fluorescence and elemental analysis techniques. Pale yellow crystals crystallize in orthorhombic system, space group *Fdd2* with *a* = 11.2368(6), *b* = 38.280(2), *c* = 10.5682(6) Å, *V* = 4545.9(4) Å³, C₁₁H₇MnN₄O₂, *M_r* = 282.15, *D_c* = 1.649 g/cm³, *μ*(MoKα) = 1.159 mm⁻¹, *F*(000) = 2272, *Z* = 16, the final *R* = 0.0613 and *wR* = 0.1773 for 2856 observed reflections (*I* > 2σ(*I*)). It shows a two-dimensional network structure and is further assembled into a three-dimensional supramolecular framework via hydrogen bonds and abundant π-π interactions. In addition, we analyzed natural bond orbital (NBO) of **1** in using the PBE0/LANL2DZ method established in Gaussian 03 Program. There is obvious covalent interaction between the coordinated atoms and Mn(II) ions.

Keywords: coordination polymer, mixed ligands, hydrothermal synthesis, crystal structure, fluorescent property, natural bond orbital; DOI: 10.14102/j.cnki.0254-5861.2011-3013

1 INTRODUCTION

The crystal engineering of metal coordination polymers (MCPs) is one of the most rapidly developing areas of chemical science owing to their diversity of type and physical-chemical properties^[1]. Obviously, it is the important responsibility for chemists to rationally design and synthesize more MCPs with diverse structures. It is well known that the assembly processes and structures of MCPs are influenced by many factors, such as the coordination preferences of metal ions^[2-4], the conformation of bridging ligands^[5], solvent systems^[6], counteranion^[7] and pH value of the solution^[8].

Considering all the aspects stated above, we aim to prepare and inquire into a new complex by carefully selecting two kinds of ligands: (a) A 2,2'-bipyridyl-like chelating ligand, 3-(2-pyridyl)pyrazole (HL), with a N-H entity as a hydrogen-bonding donor^[9-11], has become one of the hot topics of new drug research because of its broad-spectrum biological activity, and shows broad applications in the field of agricultural production, (b) pyrazine-2,3-dicarboxylic acid

(H₂pzdc), with O and N donor atoms^[12]. In this manuscript, a new Mn(II) coordination complex with these ligands, [Mn(pzdc)_{0.5}(L)]_n (**1**), was synthesized and structurally determined by X-ray analysis. It exhibits a two-dimensional network structure and further extends into a 3D supramolecular structure through C-H··O, C-H··N hydrogen bonds and π-π interactions.

2 EXPERIMENTAL

2.1 Materials and methods

All starting materials from commercial sources were of reagent grade and used directly without further purification. The elemental analysis (C, N, H) was carried out on a PE 240C elemental analyzer, and FT-IR spectra were recorded on a Tensor 27 OPUS (Bruker) FT-IR spectrometer with KBr pellets. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Ultima IV X-ray diffractometer with CuKα radiation (λ = 1.5418 Å) at 40 kV and 40 mA within 5° to 50° (2θ). Thermal stability (TG-DTA) was studied on a Dupont

Received 23 October 2020; accepted 8 January 2021 (CCDC 2020722)

① The project was supported by Jilin Science and Technology Development Program (JJKH20180776KJ) and Jilin Normal University Graduate Innovation Program (201939)

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thermal analyzer from room temperature to 800 °C. The luminescent spectra for polycrystalline samples were measured at room temperature on a Hitachi F-7000 fluorescence spectrometer with a xenon arc lamp as the light source.

2.2 Synthesis

Pzdc (0.2 mmol, 33.6 mg), Mn(OAc)₂·4H₂O (0.2 mmol, 49.0 mg), HL (0.2 mmol, 29.0 mg) and 15 mL H₂O being weighed accurately, this solution was put in a steel reactor with 25 mL PTFE lining after adding an appropriate amount of trimethylamine and adjusting the pH value to 8.10. The reactor was placed in a 170 °C oven for 120 h, and then cooled down at a rate of 5 °C h⁻¹. The resulting mixture was filtered to separate out the pale yellow block crystals which were washed with water and air-dried (Yield: 21%). Elemental analysis (wt%) calcd. for C₁₁H₇MnN₄O₂ (*M_r* = 282.15): C, 46.83; H, 2.50; N, 19.86%. Found: C, 46.11; H, 2.04; N, 19.03%. IR(cm⁻¹): 3609(w), 3480(w), 3081(w), 1629(s), 1601(s), 1567(w), 1519(m), 1452(w), 1431(m),

1378(w), 1365(m), 1350(m), 1278(w), 1231(w), 1201(w), 1156(w), 1121(s), 1074(w), 978(w), 880(w), 851(w), 753(s), 694(w), 670(w), 638(w), 567(w), 474(w), 444(w).

2.3 Determination of the crystal structure

Suitable single crystals of complex **1** were carefully selected under an optical microscope for data collection which was performed on a Bruker Smart Apex II CCD diffractometer with graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å) by using an ω -scan mode at room temperature. The raw data frames were intergrated into SHELX-format reflection files and corrected using the SAINT program. Absorption corrections based on multiscan were obtained using the SADABS program. All the structures were solved by direct methods and refined with full-matrix least-square on *F*² using SHELXL 97^[13, 14]. Hydrogen atoms were located by geometric calculations and their positions and thermal parameters were fixed during the structure refinement. Crystal data (bond lengths and angles) parameters for complex **1** are listed in Table 1.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for **1**

Bond	Dist.	Bond	Dist.	Bond	Dist.
Mn(1)–O(2A)	2.274(7)	Mn(1)–N(1)	2.369(7)	Mn(1)–N(2)	2.284(7)
Mn(1)–N(3B)	2.269(8)	Mn(1)–N(4)	2.374(7)		
Angle	(°)	Angle	(°)	Angle	(°)
N(3B)–Mn(1)–N(2)	96.3(3)	O(2A)–Mn(1)–N(2)	88.4(3)	N(3B)–Mn(1)–N(1)	160.7(4)
O(2A)–Mn(1)–N(1)	92.0(4)	N(2)–Mn(1)–N(1)	71.8(3)	N(3B)–Mn(1)–N(4)	97.4(3)
O(2A)–Mn(1)–N(4)	101.1(3)	N(2)–Mn(1)–N(4)	161.2(3)	N(1)–Mn(1)–N(4)	91.4(3)

Symmetry codes: A: $-x+3/2, -y, z-1/2$; B: $-x+1, -y, z$

3 RESULTS AND DISCUSSION

3.1 Structural description

X-ray analysis reveals that complex **1**, [Mn(pzdc)_{0.5}(L)]_{*n*}, consists of divalent Mn²⁺ ion, half pzdc²⁻ anion and a L ligand, as shown in Fig. 1, which also shows the coordination environments of the Mn(II) ions and the ligands. Each penta-coordinated Mn(II) ion in **1** is surrounded by three N atoms from two chelating L ligands, one N atom and one oxygen atom from the bridging pzdc²⁻ anion, in which the Mn(1)–O bond length is 2.274(7) Å and the Mn(1)–N bond lengths are in the range of 2.269(8)~2.374(7) Å. The coordination angles around the Mn(II) ion vary from 67.3(3) to 160.7(4)°.

In complex **1**, each pzdc²⁻ ligand adopts the μ_4 coordination mode, acting as a μ_4 -bridge to link four Mn(1) ions, forming a two-dimensional network (Fig. 2). Meanwhile, each L ligand

adopts the μ_3 chelating coordination mode. In the complex, one kind of C–H··O hydrogen bonds with C··O distances of 3.142(17) Å and another kind of C–H··N hydrogen bonds with C··N distances of 3.457(18) Å are present: (a) hydrogen bonds between pyrazine carbon atom and carboxylate O atom; (b) hydrogen bonds between pyrazine carbon and pyrazol N atoms. In addition, there are π - π stacking interactions among parallel pyridine rings of L ligands. The centroid-to-centroid distance is 3.926(7) Å for N(1)C(1)C(2)C(3)C(4)C(5) and N(1')C(1')C(2')C(3')C(4')C(5') rings ($1/4 + x, 7/4 - y, -1/4 + z$), with the vertical distance to be 3.470(5) Å, indicating the existence of significant π - π effect (Fig. 3), thus making the structure more stable. Therefore, an interesting three-dimensional supramolecular network structure is formed via abundant hydrogen-bonding and π - π stacking.

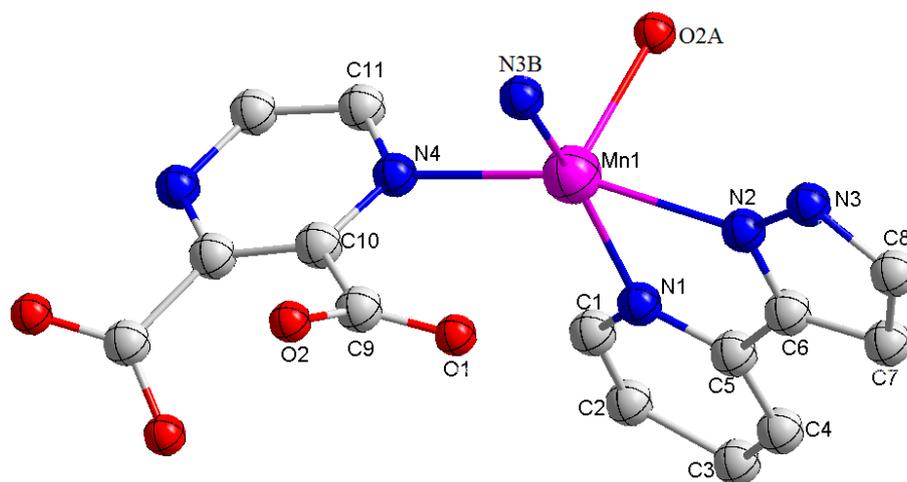


Fig. 1. Coordination environment of the Mn(II) center in **1** (Symmetry codes: (A) $-x+3/2, -y, z-1/2$ (B) $-x+1, -y, z$)

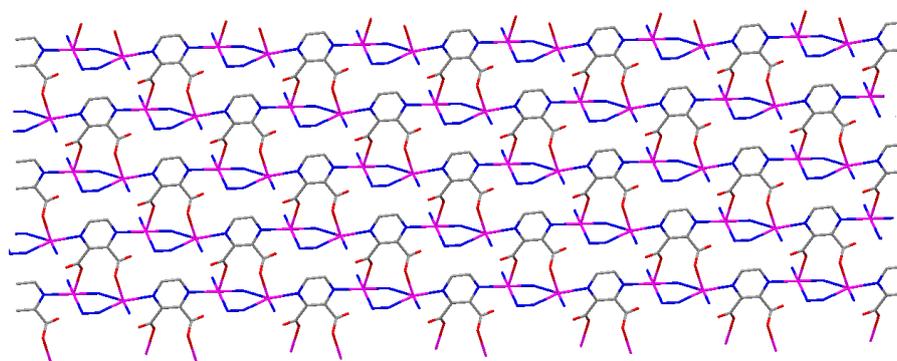


Fig. 2. View of the two-dimensional network structure (Carbon atoms of HL ligand were omitted for clarity)

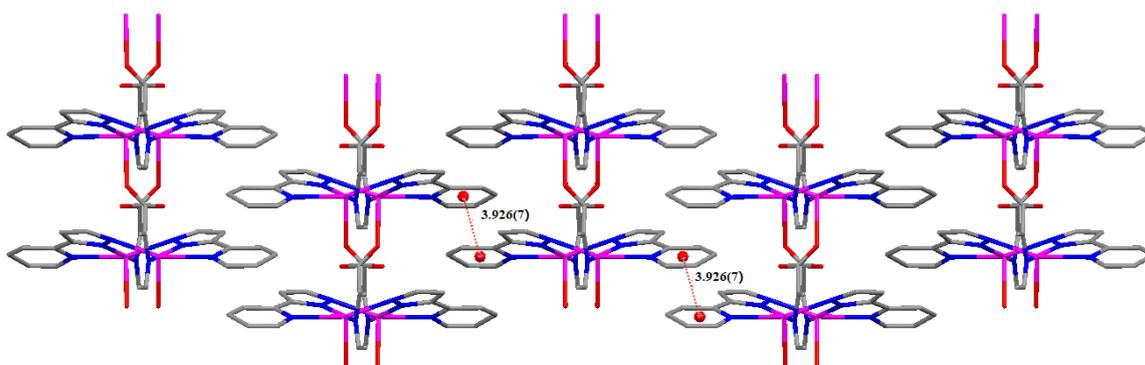


Fig. 3. View of π - π interactions in **1** (The dotted lines show π - π interactions)

3.2 IR analysis

The IR spectra of complex **1** with the frequency range of $400\sim 4000\text{ cm}^{-1}$ are shown in Fig. 4. There is no absorption peak between 1730 and 1670 cm^{-1} , indicating that carboxyl groups of the organic moieties in **1** are deprotonated^[15]. The peaks at 1601 and 1452 cm^{-1} are assigned to the stretching bands of $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, respectively, and the strong bands at 753 cm^{-1} to the $\nu_{(\text{C}-\text{N})}$ stretching of N-heterocyclic rings of the pzdc and L ligands.

3.3 Powder X-ray diffraction (PXRD)

PXRD analyses of complex **1** were carried out at room temperature (Fig. 5). The experimental PXRD patterns are closely matched with those in the simulated ones from single-crystal structures, revealing the phase purity of the bulk crystalline materials.

3.4 Thermogravimetric analysis

Complex **1** is stable under room environmental conditions, and thermogravimetric experiment was carried to investigate its thermal stability. For **1**, the first weight loss of 26.52% occurs from 242 to $295\text{ }^\circ\text{C}$ attributed to the departure of

coordinated pzdc ligand (calcd. 25.18%), and the second of 56.13% from 295 to 540 °C results from the loss of L ligand (calcd. 55.34%). The remaining weight, 26.6%, corresponds

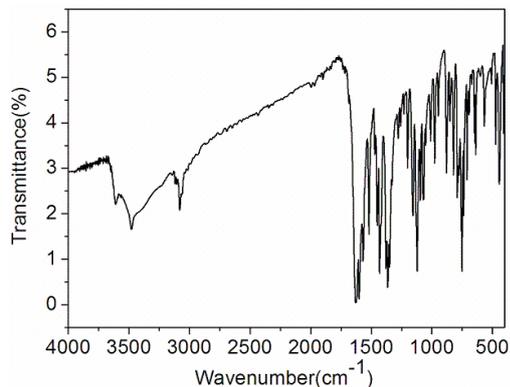


Fig. 4. IR spectrum of complex 1

to the Mn and O percentage (25.14%), indicating that the final product is MnO (Fig. 6).

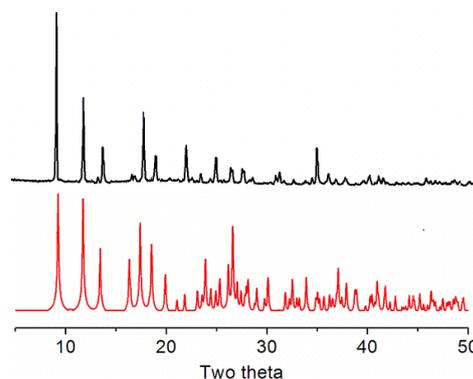


Fig. 5. PXRD analysis of 1: bottom-simulated, top-experimental

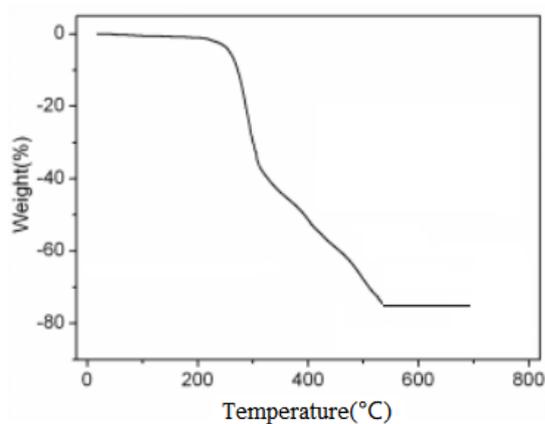


Fig. 6. TG curve of 1

3.5 Photoluminescent properties

The luminescent property of complex **1** in the solid state at room temperature was measured, as shown in Fig. 7. Upon excitation at 355 nm, the emission of the complex is at 454 nm, which falls in the blue spectral range. Then we studied the photoluminescence properties of free L and H₂pzdc ligands, and verified that they do not emit any luminescence in the range of 400~800 nm. The emissions of complex **1** may be vested in the ligand-to-metal charge-transfer (LMCT)^[16, 17].

4 THEORETICAL CALCULATIONS

The presented calculations were performed with the Gaussian03 program^[18]. Experimental data of the complex **1** provided the start geometries of the molecular structure for calculation. We analyzed the NBO by DFT^[19] with the PBE0^[20, 21] hybrid functional and the LANL2DZ basis set^[22-24]. One Mn(II) ion, one pzdc ligand and one L ligand

were selected as unit structures of calculation.

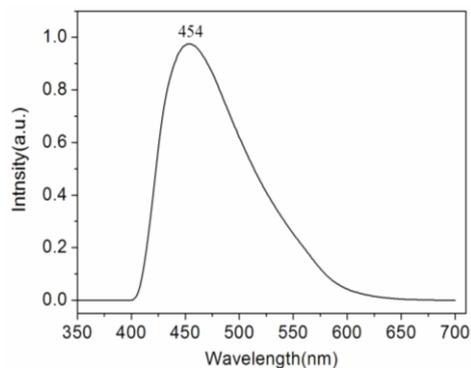


Fig. 7. Solid-state emission spectrum of **1** at room temperature

The major natural atomic charges, natural electron configuration, Wiberg bond index and NBO bond orders (a.u) for **1** are listed in Table 3 with the electronic configuration of Mn(II) ion, N, and O atoms being $4s^{0.24}3d^{5.31}4p^{0.38}$, $2s^{1.29\sim 1.36}2p^{3.90\sim 4.14}$ and $2s^{1.67}2p^{4.93\sim 5.00}$, respectively. One can deduce

that the Mn(II) ion coordination with N and O atoms is mainly on $3d$, $4s$ and $4p$ orbitals. The coordination bonds with Mn(II) ion were formed with $2s$ and $2p$ orbitals, and Mn(II) ion obtained electrons from four N atoms of L ligand and one O atom of pzdc ligand^[23, 24]. According to

valence-bond theory, the atomic net charge distribution and the NBO bond orders of complex **1** (Table 2) display the manifest covalent interaction between Mn(II) and its coordination partners.

Table 2. Natural Atomic Charges, Natural Valence Electron Configuration, Wiberg Bond Index and NBO Bond Order (a.u.) for **1**

Atom	Net charge	Electron configuration	Bond	Wiberg bond index	NBO bond order
Mn(1)	1.05808	[core]4s(0.24)3d(5.31)4p(0.38)			
O(2A)	-0.67923	[core]2s(1.67)2p(5.00)	Mn(1)-O(2A)	0.3326	0.2923
N(1)	-0.47292	[core]2s(1.32)2p(4.14)	Mn(1)-N(1)	0.3291	0.3050
N(2)	-0.27623	[core]2s(1.29)2p(3.96)	Mn(1)-N(2)	0.3735	0.3394
N(3B)	-0.27860	[core]2s(1.35)2p(3.90)	Mn(1)-N(3B)	0.3446	0.3359
N(4)	-0.48767	[core]2s(1.36)2p(4.11)	Mn(1)-N(4)	0.2536	0.2819

It can be seen from Fig. 8, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) are mainly located on the L ligand.

Therefore, ILCT (intraligand charge-transfer) can be deduced from some profiles of molecular orbital of complex **1**.

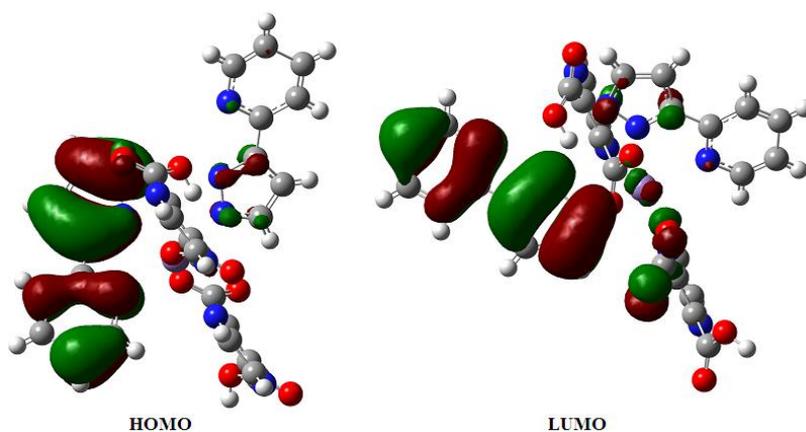


Fig. 8. Frontier molecular orbitals of complex **1**

5 CONCLUSION

A new complex by using different N-donor auxiliary ligand L and O-donor pzdc and metal salts, was successfully obtained. The pzdc ligand employs monodentate bridging modes, while the L ligand exhibits μ_3 chelating coordination

mode and connects the surrounding Mn(II) ions to generate a 2D network. In the meantime, a 3D supramolecular architecture is formed through abundant hydrogen bonding and π - π stacking interactions. A NBO study confirms the manifest covalent interaction between the Mn(II) ion and its coordination partners.

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