



Synthesis, Structure, Luminescence and Thermal Stable Properties of Zn(II) Coordination Polymer Constructed from 2-Hydroxyphenylacetic Acid and 4,4'-Trimethylenedipyridine†

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A novel complex **1** of $[\text{Zn}(\text{tdp})(\text{dpa})_2]_n$ (Hdpa: 2-hydroxyphenylacetic acid; tdp: 4,4'-trimethylenedipyridine) was prepared and characterized by elemental analysis, IR, TGA, X-ray single crystal diffraction. The carboxylate oxygens of the 2-hydroxyphenylacetic acid (Hdpa) ligands connect one Zn(II) ion in monodentate coordinated modes to form mononuclear zinc(II) building blocks, which are further linked into a 1D infinite chain through *trans*-tdp ligands. Furthermore, the luminescent properties of **1** was also investigated.

Keywords: Zn(II) coordinated polymer, Crystal structure, Luminescence.

INTRODUCTION

Molecular self-assembly of hybrid inorganic-organic architectures is a rapidly developing indagate field of crystal engineering and coordination chemistry¹⁻⁵. The self-assembly of complexes is effected by much factors, howbeit, policy synthesis or choice of the ligand are key factors for acquireing expected complexes⁶⁻¹⁰. The aromatic carboxylate ligands are most favoured because of their strong coordinating abilities¹¹⁻¹³. Moreover, the pliable 4,4'-trimethylenedipyridine ligand is an outstanding candidate to build novel structures as the accessorial ligands¹⁴⁻¹⁷. The aromatic carboxylate ligand of hydroxyphenylacetic acid to build various complexes may result in some tailorable structures¹⁸⁻²⁰. So far, work on the molecular assembly of metals coordination architectures involving 2-hydroxyphenylacetic acid (Hdpa) ligand and N-containing auxiliary ligands is still scarce. In this study, we introduced 2-hydroxyphenylacetic acid (Hdpa) together with the 4,4'-trimethylenedipyridine (tdp) for preparation of the zinc ion complex $[\text{Zn}(\text{tdp})(\text{dpa})_2]_n$ (**1**). In addition, IR, TGA and luminescent of **1** were discussed.

EXPERIMENTAL

All the reagents were of reagent grade. C, H and N EA (elemental analysis) was performed on a CARLO ERBA 1106 analyzer, it shows the percentage of carbon, hydrogen and

nitrogen of the complexes. IR spectra were carried out on a Bruker FTIR-55 spectrometer using KBr pellets at a resolution of 0.5 cm^{-1} ($4000-400 \text{ cm}^{-1}$). The luminescence spectra studies were carried at room temperature on a PE (PerkinElmer) LS 55 phosphorimeter. TG-DTA was performed on a PE (PerkinElmer) TG/DTA 6300 under flowing N_2 atmosphere at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ in the temperature range $20-800 \text{ }^\circ\text{C}$.

General procedure: To the solution of a zinc nitrate (0.145 g, 0.5 mmol), 2-hydroxyphenylacetic acid (0.076 g, 0.5 mmol) and 4,4'-trimethylenedipyridine (0.0991 g, 0.5 mmol) were dissolved in 1:1 water/methanol solution and the pH was adjusted to 7 with 0.1 M potassium hydroxide solution. The mixture was stirred for 0.5 h, the precipitate was dissolved an aqueous NH_3 solution (14 M) was added drop by drop into the mixture to give a clear solution. After 3 weeks, colourless crystals were obtained by evaporation at room temperature in 56.5 % yield (based on Zn). Anal. calcd. (%) for $\text{C}_{29}\text{H}_{28}\text{N}_2\text{O}_6\text{Zn}$: C 61.01, H 4.65, N 4.64; found (%): C 61.55, H 4.99, N 4.95. IR (KBr pellet, cm^{-1}): 3429 (w), 3164 (w), 2373 (w), 1655 (s), 1622 (s), 1577(s), 1499 (m), 1435 (m), 1409 (m), 1338 (m), 1253 (m), 1150 (w), 1066 (w), 1027 (m), 806 (m), 755 (m), 709 (w), 658 (w).

Detection method: Data collection was performed on a Bruker SMART APEXII CCD²¹ diffractometer operating a MoK_α radiation ($\lambda = 0.071073 \text{ nm}$) by using an ω scan mode and scanning scope of $2.49^\circ \leq \theta \leq 25.00^\circ$ at $295(2) \text{ K}$. All

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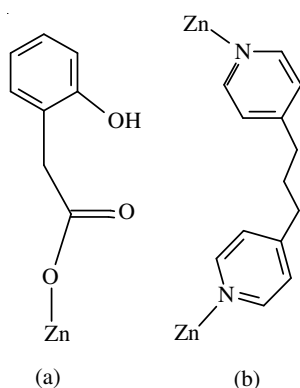
TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENTS OF COMPLEX 1

Empirical formula	C ₂₉ H ₂₈ N ₂ O ₆ Zn	γ (°)	101.271(2)
Formula weight	565.90	V (Å ³)	1313.8(4)
Temperature (K)	296(2)	Z	2
Size (mm)	0.30 × 0.20 × 0.18	μ (mm ⁻¹)	0.981
θ range for data collection (°)	2.49–25.00	D _c (g cm ⁻³)	1.431
Crystal system	Triclinic	F ₍₀₀₀₎	588
Space group	P-1	Reflections collected	8221
a (Å)	6.4746(13)	Independent reflections (R _{int})	4573 (0.0232)
b (Å)	12.940(3)	Goodness of fit on F ²	1.075
c (Å)	17.269(3)	R ₁ , wR ² (I > 2σ(I))	0.0366, 0.1007
α (°)	109.901(2)	R ₁ , wR ₂ (all data)	0.0426, 0.1056
β (°)	95.393(2)	(Δρ) _{max} , (Δρ) _{min} /e Å ⁻³ (e nm ⁻³)	0.615, -0.652

absorption corrections were applied using the SAINT²². The structures were refined by direct methods with SHELXTL-97 package^{23,24}. R₁ = 0.0366 and wR₂ = 0.1007 (w = 1/[σ²(F_o)² + (0.0723P)² + 0.0120P] where P = (F_o² + 2F_c²)/3. S = 1.075 and (Δ/σ)_{max} = 0.000.

RESULTS AND DISCUSSION

Structure description: Each the zinc ion is covalently bound by two N-atoms of two tdp ligands and two oxygen atoms from two Hdpa ligands in the asymmetric unit of 1, displaying a distorted tetrahedron geometry. This structure is similarly adopted by [Zn(L)(BBI)·H₂O]_n (H₂L = 4-carboxymethylbenzoic acid, BBI = 1,1-(1,4-butanediyl)bis(imidazole)²⁵, {Zn(1,4-bdc)(2, 6-bip)·2H₂O}_n and {Zn(BDC)(BIP)·DMF}_n (BDC = benzenedicarboxylate, BIP = bis(imidazole-1-yl)pyridine)²⁶. The bond lengths of Zn-O [1.9458(17), 1.9658(16) Å] and Zn-N [2.0298(19), 2.0308(18) Å] are comparable to the ones found in [Zn(BDC)(BIMX)]·1.5H₂O (BDC = 1,4-benzenedicarboxylate, BIMX = bis(imidazol-1-ylmethyl)-tetramethylbenzene)²⁷. The carboxyl group of Hdpa coordinates to the zinc ion in a monodentate fashion (**Scheme-I**). The carboxyl group and a hydroxyl group of Hdpa form intramolecular hydrogen bond, with the O and O bond length of 2.667(2), 2.624(3) Å and the O-H and O bond angle of 163.4, 164.1°, respectively.



Scheme-I: Coordination mode of Hdpa and tdp ligands

Every tdp ligand bridges two neighbouring zinc ion to form a 1-D chain along and the tdp ligand has TG conformation²⁸ (**Scheme-I**). The Zn...Zn distance is 12.940 Å by the bridging tdp in complex 1, which is similar to that observed in [Zn(Hhbc)₂(bbi)]_n (Zn...Zn distance is 12.670 Å)²⁹.

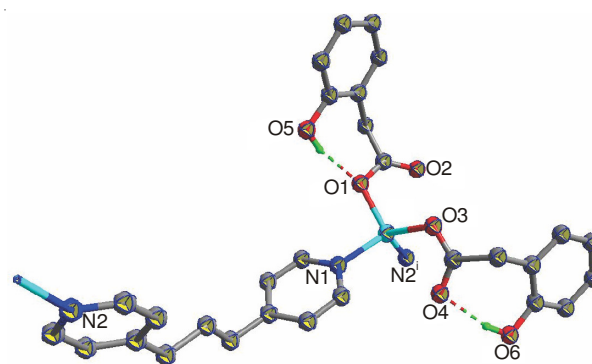


Fig. 1. Molecular structure of complex 1

TABLE-2 CONCERNMENT BOND LENGTHS (Å) AND BOND ANGLES (°)			
Zn(1)-O(3)	1.9458(17)	Zn(1)-O(1)	1.9658(16)
Zn(1)-N(1)	2.0298(19)	Zn(1)-N(2)#1	2.0308(18)
N(2)-Zn(1)#2	2.0308(18)	O(1)-C(1)	1.295(3)
O(2)-C(1)	1.211(3)	O(3)-C(9)	1.264(3)
O(4)-C(9)	1.238(3)	—	—
O(3)-Zn(1)-O(1)	113.05(7)	O(3)-Zn(1)-N(1)	116.61(8)
O(1)-Zn(1)-N(1)	99.54(7)	O(3)-Zn(1)-N(2)#1	108.67(7)
O(1)-Zn(1)-N(2)#1	109.13(7)	N(1)-Zn(1)-N(2)#1	109.42(8)

Symmetry code: #1 x, y + 1, z #2 x, y-1, z.

The reverse arrangement of Hdpa ligand one-dimensional chain on both sides, with the help of hydrogen-bonded interactions between adjacent 1D sheet [C(28)-H(28A)...O(2)#3 = 3.165(3) Å, #3 x + 1, y-1, z], the polymeric sheet are assembled to form a two-dimensional structure (Fig. 2 and Table-3).

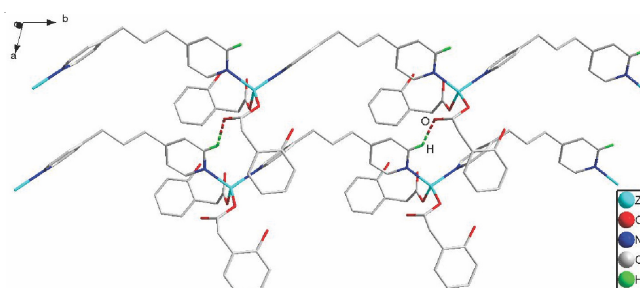


Fig. 2. Layers of the complex 1

With the help of C-H...π [C(17)-H(17A)...π = 2.664 Å] stacking interactions between adjacent the polymeric sheet are assembled to form a supramolecular 3-D network structure. (Fig. 3.)

TABLE-3 HYDROGEN BOND (H...A)/Å AND BOND ANGLES (°)		
O(5)-H(5O)...O(1)	1.87	163.4
O(6)-H(6O)...O(4)	1.83	164.1
C(18)-H(18A)...O(4)	2.48	134.7
C(28)-H(28A)...O(2)#3	2.48	130.6
C(7)-H(7A)...O(5)#4	2.43	163.8
C(4)-H(4A)...O(2)#5	2.47	156.3

Symmetry code: #3 x + 1, y - 1, z #4 -x, -y, -z + 1 #5 -x, -y + 1, -z + 1.

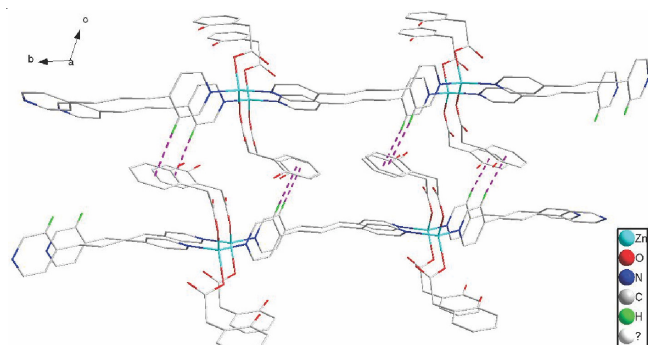


Fig. 3. 3D crystal structures complex 1

IR Spectrum: The peaks of 1622 and 1409 cm^{-1} of **1** are attributed to $\nu_{\text{as}}(\text{OCO}^{-1})$ and $\nu_{\text{s}}(\text{OCO}^{-1})$ in the IR spectra. The value of $\Delta(\text{OCO}^{-1})$ is 213 cm^{-1} , infer that the Hdpa is coordinated to the Zn(II) atom in the monodentate binding mode³⁰. Meanwhile, characteristic bands nearby 1530 cm^{-1} (1499 cm^{-1} in **1**) belong to the stretching vibration of $-\text{N}=\text{C}-$ of tdp ligands.

Thermal analysis: The thermal stability of **1** exhibits a mass loss around 173 $^{\circ}\text{C}$ and then decomposition begins (Fig. 4). This structure is similarly adopted by $[\text{Zn}(2,4\text{-D})_2(\text{ibb})]_n$ (2,4-D=2,4-dichlorophenoxyacetic acid, $\text{ibb}=1,12-(1,4\text{-butanediy})\text{bis}(\text{imidazole})$)³¹.

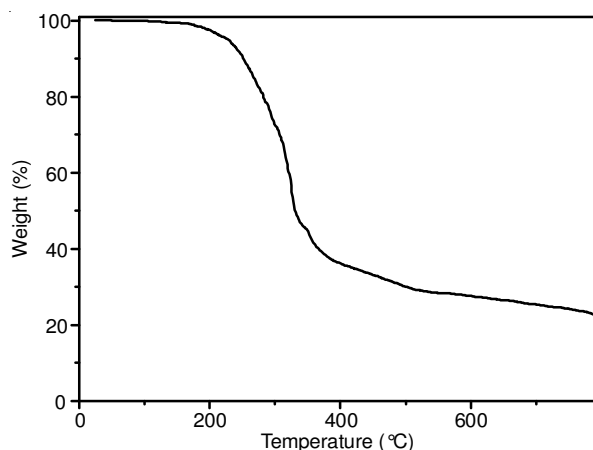


Fig. 4. Thermogravimetric curves for complex 1

Photoluminescence properties: In study of **1**, the emission peaks were not observed for free Hdpa ligands. The emission peaks at ca. 455 nm ($\lambda_{\text{ex}} = 372 \text{ nm}$)³² were observed for free tdp ligands, where most probably due to the $\pi-\pi^*$ transition. On complexation of these ligands with Zn(II) atoms, strong fluorescence with emission peak at ca. 435 nm ($\lambda_{\text{ex}} = 308 \text{ nm}$) for compound was observed at room temperature (Fig. 5). Therefore, the shows broad emission bands can probably be assigned to the ligand-to-metal charge-transfer transitions³³.

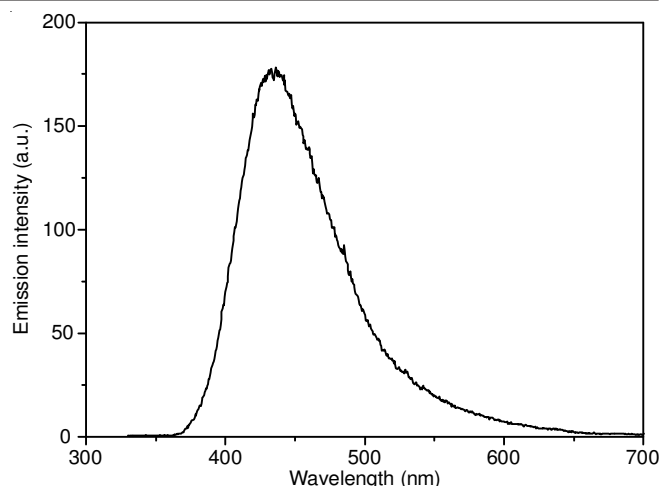


Fig. 5. Solid-state photoluminescent spectrum

Conclusion

A new 1D zinc(II) complex based on Hdpa and tdp ligands, $[\text{Zn}(\text{tdp})(\text{dpa})_2]_n$ are reported. This successful preparation of the title compound indicates that the tdp can be an outstanding proposer for the construction of coordination polymers. Complex **1** emits the intensely luminescence with the fluorescence of 435 nm.

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