



Research Article

Zinc-orotate coordination polymer: synthesis, thermogravimetric analysis and luminescence properties

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Abstract

Orotic acid formulated coordination network of formula $[Zn(HOr) \cdot 3H_2O]_n$ (**1**) prepared by reactions of orotic acid potassium salt $[K(H_2Or)]$ accompanied by metal salts $Zn(OAc)_2 \cdot 2H_2O$ at room temperature. X-ray single-crystal investigation confirms that the carbonyl oxygen of the ring in **1** is structure factor for 1D Zn-orotate coordination chain. The hydrogen bonding among uncoordinated carboxylate oxygen of ligand and one of the aqua ligand assembles the nearby parallelly stacked 1D coordination chain into 2D hydrogen bonded architecture, further hydrogen bonding among coordinated water and carbonyl oxygen incorporating O–H...O synthons yielding into 3D hydrogen bonded coordination network. O–H...O synthons were the only concoction for hydrogen bonded metal–organic network of zinc coordination polymers. The emission spectra of Zn-orotate complex shows excitation wavelength at 270 nm which depicts that **1** has strengthened photoluminescence with peak recorded of 376 nm (3.2975 eV) and is the outcomes of $n-\pi^*$ and $\pi-\pi^*$ transitions of orotate ligand. Thermal decomposition predicts that at 120 °C, lattice water molecule entirely release out from the complex, moderately degradation starts and around 370 °C the entire disintegration has been inspected.

Keywords Crystal engineering · Zn-coordination polymer · Photoluminescent property

1 Introduction

The strong coordination capability of nitrogen atoms, with most transition metal ions by coordination bonds, the N-containing heterocyclic ligands are examined most repeatedly. The abundant non-covalent peripheral recognition sites in ligands for further accumulation into higher-dimensional multifunctional supramolecular skeleton in virtue of hydrogen bonds, $\pi \cdots \pi$ stacking and van der Waals' force [1, 2] yield rigid skeleton with higher dimensional coordination polymers. Perusal of literature reveals that construction of 2D or 3D CPs can be of great significance as they are likely to afford new materials for potential applications in field such as selective gas adsorption [3–9], molecular storage [10–13], catalysis [14–17],

photochemistry [18–20], magnetism [21–24], anion exchange [25–28] and so on.

Orotic acid (H_3Or , vitamin B13) and their metal complexes go on to attract attention by the reason of its multi-dentate functionality and its huge impact in living organisms as a precursor of pyrimidine nucleosides [18–20]. Metal orotates have also caught growing acknowledgment in medicine. As a part of our continuing research on crystal engineering of metal–organic/orotate crystals comprising synthon induced molecular accumulation into higher dimensionality [29–35] in this manuscript we have reported 3D hydrogen bonded Zn-orotate network based upon potassium orotate, in which carboxylic group will be available to be coordinated to metal ion and imino and carbonyl oxygen will provides platform for non-covalent

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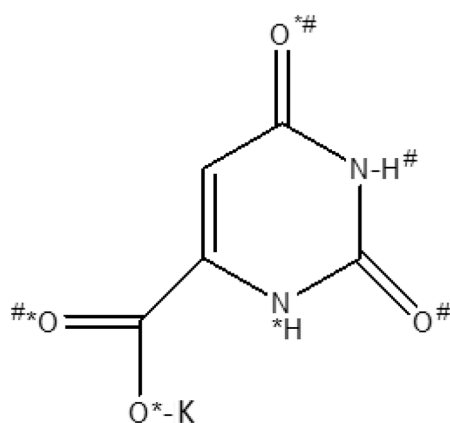
interactions (N–H...O and O–H...O synthons). Since the carbonyl group and carboxylate anion is a universal H-bond acceptor simultaneously as imino group is an H-bond donor, these peripheral groups are anticipated to interact with each other or with aqua ligand through hydrogen bonding, of pyrimidyl ring (Scheme 1).

Respectively, we have used transition metals Zn(II) ions to initiate coordination polymer that consist of pyrimidine carboxylate (Orotate) ligand which coordinated to metal ion at the pyrimidyl nitrogen and carboxylate group in $[\text{Zn}(\text{HOR})\cdot 3\text{H}_2\text{O}]_n$ (**1**). The orotate ligand coordinated the metal centre via pyrimidyl nitrogen, one carbonyl oxygen, carboxylate group, and three aqua ligands around the metal center in Zn-orotate coordination polymer. O–H...O synthons were the only contrivance for hydrogen bonded three-dimensional metal–organic framework in synthesized coordination polymers.

2 Experimental section

2.1 Material and measurements

The reagent and solvents were commercially available and were used excluding further purification zinc acetate dihydrate, orotic acid potassium salt and methanol was bought from Tokyo Chemical Industry and used as such. The C, H, and N elemental analyses were carried out with Perkin-Elmer 2400 CHN element analyzer. The FTIR spectra were recorded as KBr pellets on a Bruker Alpha spectrometer in a range of 4000–400 cm^{-1} . Powder X-ray diffraction (PXRD) patterns were obtained on a PANalytical 3 kW X'pert Powder XRD—Multifunctional with Cu K α radiation



* = Metal Binding Sites; # = Hydrogen Bonding Sites

Scheme 1 Potassium orotate exhibiting peripheral metal and H-bonding sites. *Metal binding sites; #hydrogen bonding sites

($\lambda = 1.5405 \text{ \AA}$). Thermal analysis (TG–DTA) was carried out with TGA Q500 V6.7 Build 203 instrument. Photoluminescence (PL) measurements were carried out at room temperature with an FLS980 Spectrofluorimeter (Edinburgh Instruments) equipped with a continuous Xe lamp and an S900 photomultiplier operating within 200–650 nm.

2.2 Synthesis of $[\text{Zn}(\text{HOR})\cdot 3\text{H}_2\text{O}]_n$ (**1**)

0.077 mmol (15 mg) of potassium orotate and 0.087 mmol (15 mg) of 5-amino orotic acid were dissolved, in warm solution mixture of 4 ml of deionized water and 1 ml of methanol in a conical flask. Then to 1 ml aqueous solution of zinc acetate dihydrate (0.182 mmol, 40 mg), created ligand mixture was added dropwise. The prepared mixture was cool down for crystallization at room temperature. Block crystals having yellow of **1** were collected later 3 months, relevant for X-ray diffraction. Anal. Calcd for $\text{C}_5\text{H}_8\text{N}_2\text{O}_7\text{Zn}$ (%): C, 21.95; H, 2.94; N, 10.24; Zn, 23.90. Found (%): C, 21.84; H, 3.05; N, 10.16; Zn, 23.82.

2.3 Crystal structure determinations

The data collections of **1** with a magnitude 0.569 mm \times 0.454 mm \times 0.333 mm was carried out on Bruker PHOTON detector (fine-focus sealed tube equipped radiation source) with a graphite monochromatized Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The unit cell magnitude and measurement of intensity data were taken at 100 (2) K.

The architecture was calculated by the direct methods, and accomplished by the full-matrix least-squares based on F^2 with anisotropic thermal parameters for the non-hydrogen atoms Bruker APEX2 (data collection), Bruker SAINT (cell refinement and data reduction) SHELXS-97 (structure solution), and SHELXL-97 (structure refinement) and Bruker SHELXTL (molecular graphics) [36–39]. A multi-scan adsorption correction (SADABS) was applied for **1**. Hydrogen atoms were enclosed in geometrically calculated positions using a riding model. Lattice parameters of **1** are tabulated in Table 1.

3 Results and discussion

The synthesized zinc-orotate complex was found to be insoluble in common organic solvents (ethanol, acetonitrile, acetone, DMF, chloroform) and water, were investigated by X-ray single-crystal and further corroborated by Thermal analysis, and photoluminescent property.

Orotic acid is having three metal coordination sites—(1) Carboxylic group, (2) imine nitrogen and (3) Carbonyl oxygen and four peripheral hydrogen bonding sites—(1)

Table 1 Lattice parameters of $[\text{Zn}(\text{HOR})\cdot 3\text{H}_2\text{O}]_n$ (**1**)

Molecular formula	$\text{C}_5 \text{H}_8 \text{N}_2 \text{O}_7 \text{Zn}$
Formula weight	273.50
Wavelength (\AA)	0.71073
Temperature (K)	100 (2)
Radiation type	MoK α
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
<i>Unit cell dimensions</i>	
a (\AA)	7.7254 (8)
b (\AA)	7.7854 (8)
c (\AA)	14.7445 (15)
α ($^\circ$)	90.00
β ($^\circ$)	90.00
γ ($^\circ$)	90.00
Volume (\AA^3)	886.81 (16)
Density (gm cm^{-3})	2.049
Absorption coefficient (mm^{-1})	2.792
GOF	1.094
F(000)	552
Theta range for data collection ($^\circ$)	26.00
Refinement method	Multi-scan
Limiting indices	$-9 \leq h \leq 9,$ $-9 \leq k \leq 9,$ $-17 \leq l \leq 17$
Z	4
R-factor (%)	1.32
T_{\min}, T_{\max}	0.300, 0.457

uncoordinated carboxylate oxygen, (2) two carbonyl oxygen and (3) one uncoordinated imine nitrogen (Scheme 1). As far as coordination is concerned, carboxylate and imine coordination is common to 1D Zn coordination polymer. The propagation of Zn-orotate moiety in **1** is due to

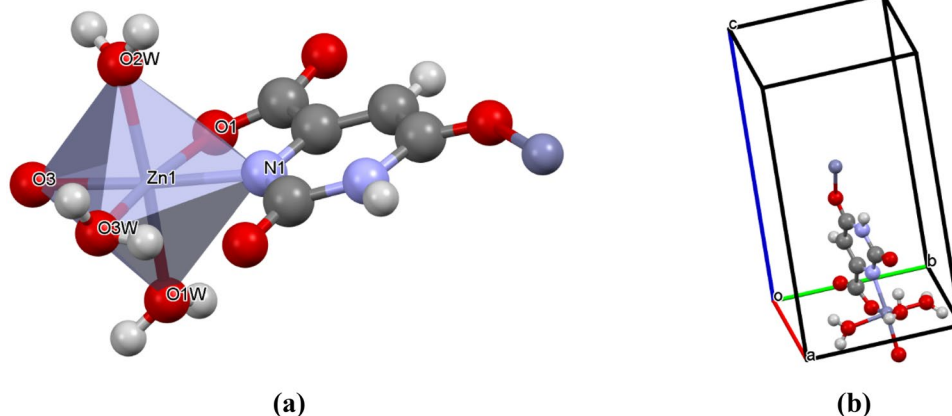
bridging of carboxylate oxygen and the role of carbonyl oxygen is appreciable for elevation of dimensionality.

3.1 Structural description of $[\text{Zn}(\text{HOR})\cdot 3\text{H}_2\text{O}]_n$ (**1**)

X-ray single-crystal diffraction investigation confirms that **1** crystallized in orthorhombic system with space group $P2_12_12_1$ (space group number 19). The asymmetric unit of zinc-orotate moiety contains metal center sites which are coordinatively saturated by orotate ion and water molecules (Fig. 1). The metal center in the coordination polymer is bonded horizontally via carboxylate oxygen atom (O1), pyrimidyl nitrogen (N1) atom, carbonyl oxygen (O3) atom and one water ligand (O3w), whereas two axial water ligands (O2w, O1w) complete the octahedral environment and Zn sites exhibits “[5 + 1]” distorted octahedral geometry. The substituted pyrimidyl ring in **1** is coplanar with the ligand with $\phi = 0^\circ$. It displays pi-pi stacking among pyrimidyl ring of adjacent molecules as shown in Fig. 2. The distances between pyrimidyl nitrogen (N1) to adjacent pyrimidyl nitrogen (N1) is 7.785 \AA .

In Zn-orotate coordination polymer, the coordination of two axial aqua ligand (O1w, O2w) and carboxylate oxygen (O1) and one aqua ligand (O3w) results in the formation of two symmetrical axis O1w–Zn–O2w, O1–Zn–O3w respectively. The carbonyl oxygen atom (O3) and pyrimidyl nitrogen (N1) (Zn1–N1 = 2.101 (2) \AA) of Orotate ring describe the third axis, O3–Zn–N1. The Zn–Ow distance for all three aqua ligand (Zn–O1w = 2.0969 (17) \AA , Zn–O2w = 2.0868 (19) \AA , Zn–O3w = 2.073 (2) \AA) and Zn–O distance of coordinated carbonyl oxygen (Zn–O3 = 2.1128 (17) \AA) is shorter than Zn–O distance of coordinated carboxylate (Zn–O1 = 2.135 (2) \AA). Other selected bond lengths and bond angles for **1** are described in Table 2.

Fig. 1 **a** The coordination sphere around Zn(II) ion and lattice water molecule in **1**, **b** Unit cell diagram of **1**



3.2 Description of hydrogen bonded coordination framework in $[\text{Zn}(\text{HOr})\cdot 3\text{H}_2\text{O}]_n$ (**1**)

The intermolecular covalent connectivity via carbonyl oxygen (O3) of Zn-orotate moiety results in the evolution of 1D coordination polymer along *b*-axis (Fig. 3). The hydrogen bonding interactions between H1w hydrogen of coordinated water (O2w) with uncoordinated carboxylate oxygen (O2) ($\text{H1w}\cdots\text{O2} = 1.866 \text{ \AA}$) between 1D chains yields 2D hydrogen bonded coordination polymer (Fig. 4) involving O–H \cdots O synthon as non-covalent connector. Hydrogen bonding parameters are listed in Table 3. As depicted from Fig. 5, the 1D chains and hydrogen bonding between them in 2D network occurs along 2_1 screw axis.

It is clear from the crystal framework that the coordinated water molecules of 1D chain are arranged along 2_1 screw axis (Fig. 4) and it is a major structure factor

for elevation of dimensionality in discussed Zn-orotate coordination polymer. All three coordinated aqua ligand actively (two axial O1w and O2w) and (one basal (O3w) takes part in hydrogen bonding. The contribution in hydrogen bonding by imine nitrogen (N2) is untouched. The uncoordinated carboxylate oxygen (O2) act as bifurcated acceptor and form hydrogen bond with H1w2 hydrogen of coordinated water (O2W) ($\text{H1w}-\text{O2} = 1.866 \text{ \AA}$) while H2w2 forms hydrogen bond with carbonyl oxygen (O4 of ring) ($\text{H2w}-\text{O4} = 1.809 \text{ \AA}$) down to *a* axis and extending the network along the *bc* plane subsequent in the evolution of 3D hydrogen bonded framework (Fig. 6).

The uncoordinated carbonyl oxygen and carboxylate oxygen of orotate ion is key non-covalent connector in self-assembly of Zn-orotate based 2D network through hydrogen bonded synthon (O–H \cdots O) and is also the only

Fig. 2 π - π Interactions in Zn-orotate complexes with pyrimidyl-based ligands ($\phi = \theta^\circ$)

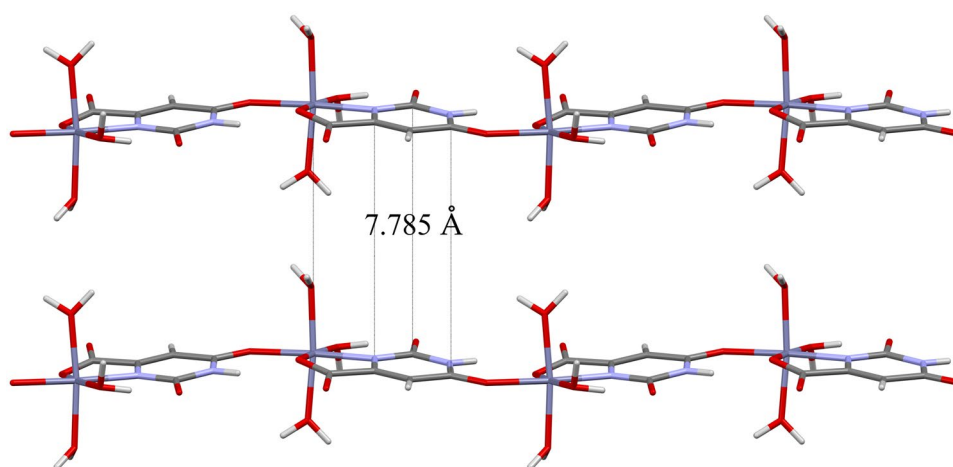


Table 2 Selected bond angles and lengths in 1 (Å) and ($^\circ$)

Zn1–O3W	2.073 (2)	Zn1–O2W	2.0868 (19)	Zn1–O1W	2.0969 (17)
Zn1–N1	2.101 (2)	Zn1–O3	2.1128 (17)	Zn1–O1	2.135 (2)
O3W–Zn1–O2W	93.86 (8)	O3W–Zn1–O1W	89.50 (7)	O2W–Zn1–O1W	173.48 (8)
O3W–Zn1–N1	93.73 (7)	O2W–Zn1–N1	91.26 (8)	O1W–Zn1–N1	94.10 (8)
O3W–Zn1–O3	90.22 (7)	O2W–Zn1–O3	86.27 (8)	O1W–Zn1–O3	88.14 (7)
N1–Zn1–O3	175.48 (8)	O3W–Zn1–O1	171.54 (7)	O2W–Zn1–O1	87.08 (8)
O1W–Zn1–O1	90.42 (7)	N1–Zn1–O1	77.84 (7)	O3–Zn1–O1	98.23 (6)

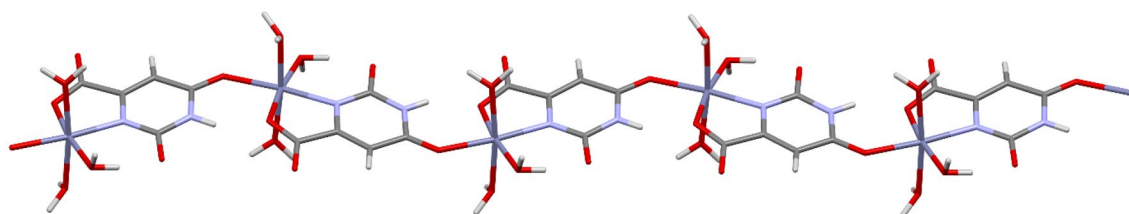


Fig. 3 The crystal network in **1** showing 1D polymeric layer of Zn-orotate down to crystallographically "*b*" axis

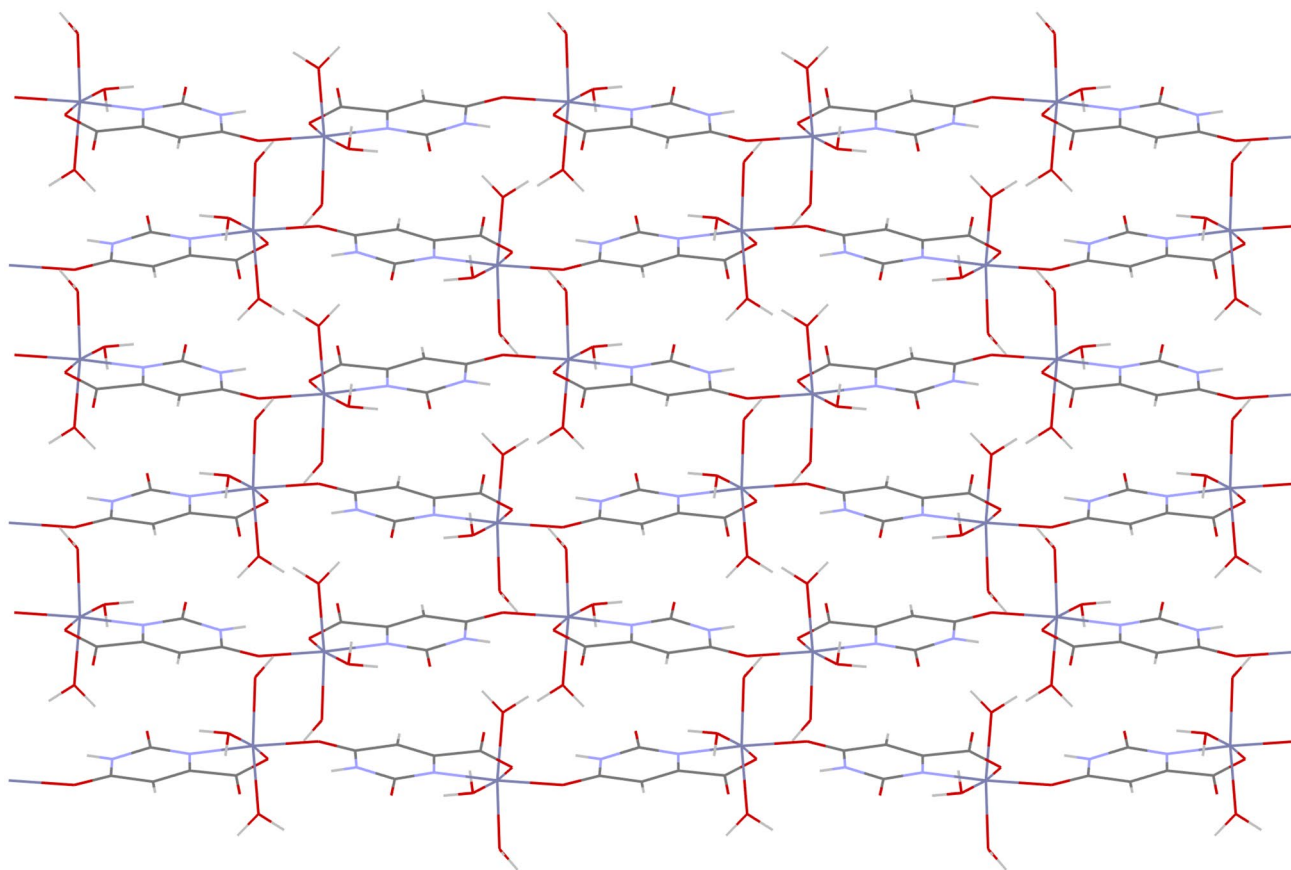


Fig. 4 View of the crystal network in **1** down to crystallographically “*b*” axis showing parallel 1D chain. Note coordinated water molecules of nearby 1D chain are arranged along 2_1 screw axis

Table 3 Conventional hydrogen bonding parameters for **1** (Å) and (°)

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O2w–2H...O4	0.916	1.809	2.675	156.61
O2w–1H...O2	0.916	1.866	2.781	177.32
O3w–2H...O2	0.942	1.847	2.750	159.64
O1w–2H...O3	0.901	1.949	2.841	170.26
O1w–1H...O1	0.933	2.150	2.966	145.44

structure factor for higher dimensionality (3D) in reported H-bonded Zn–HO_r coordination polymer.

3.3 FTIR, PXRD and thermogravimetric analysis

In Fig. 7 shown the FTIR spectra of K(H₂Or) and Zn-*orotate*. As shown Fig. 6, It can be observed that the stretching

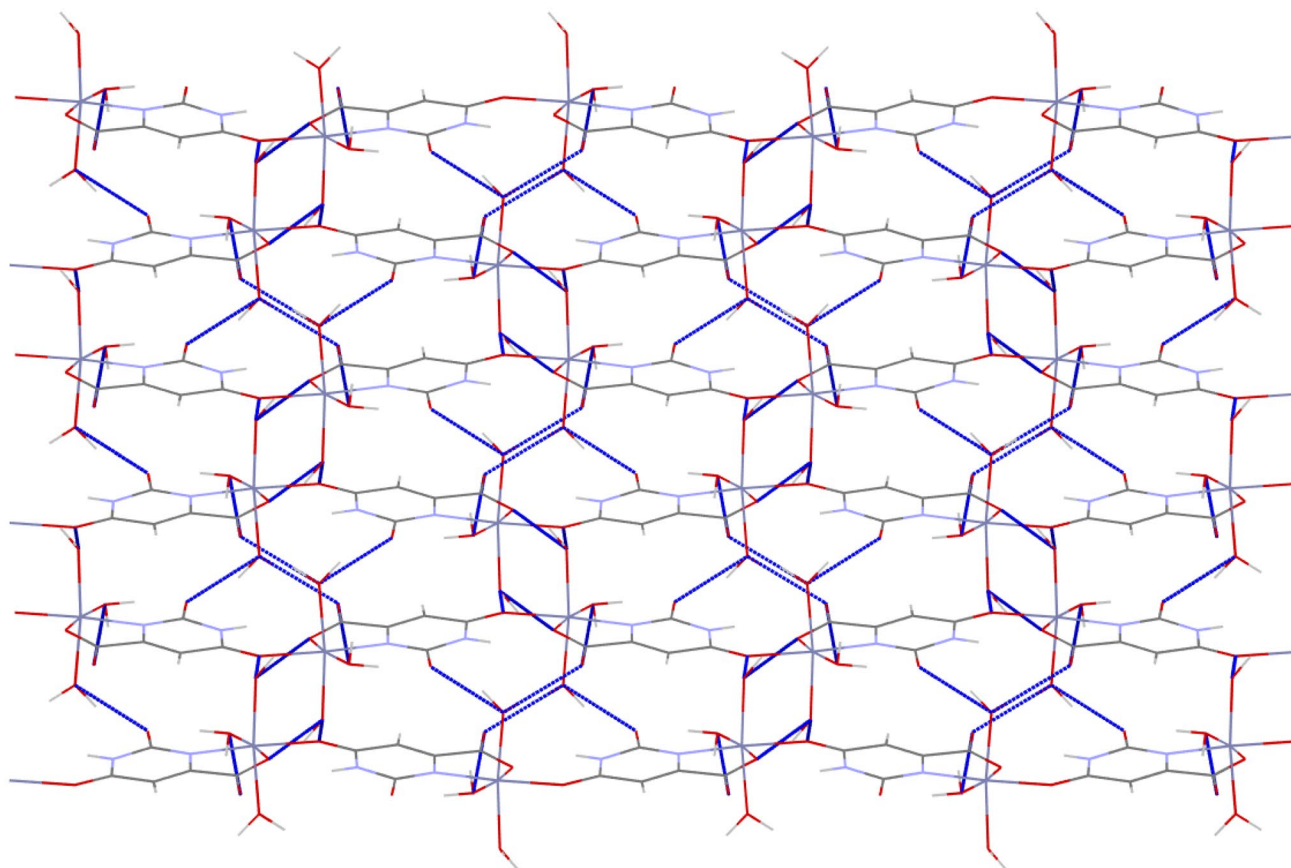


Fig. 5 View of crystal structure down to crystallographically “*b*” axis showing 2D Hydrogen bonded coordination polymer involving bifurcated hydrogen bonding interactions between H1w hydrogen

of coordinated aqua (O2w) with uncoordinated carboxylate oxygen (O2) and free carbonyl oxygen (O4) of pyrimidyl ring

vibration peak and symmetric stretching vibration peak of COOH group for $K(H_2O)_2$ were transferred from 3468.64 and 1378.10 to 3436.56 and 1384.60 cm^{-1} , respectively, after formation of Zn complex. In Zn-oxalate complex a peak at 1637.78 cm^{-1} corresponding to $(-NH-CO-)$ group [40]. At room temperature, Fig. 8 shown the phase purity of complex **1** was recorded by PXRD pattern of the bulk sample, which could be indexed to the simulated pattern, indicating that the complex is in pure phase. The slight differences in intensity may be due to the preferred orientation of the sample. The thermal stability of **1** is depicted

in Fig. 9, 4.3410 mg of Zn-oxalate was evaluated by thermogravimetric analysis (TGA) from room temperature to 800 °C under 20 ml min^{-1} of flowing nitrogen gas atmosphere. As indicated from thermogravimetric curve up to 100 °C no weight loss takes place in Zn-oxalate network. As temperature proceeds to higher degree the weight loss begins. The loss of coordinated water molecules started around 110 °C. All three coordinated molecules get dehydrated at 330 °C. Completion of dehydration as a consequence, the complex exhibits a slight plateau nearby 370 °C and over that temperature disintegration of the complex emerges (Scheme 2).

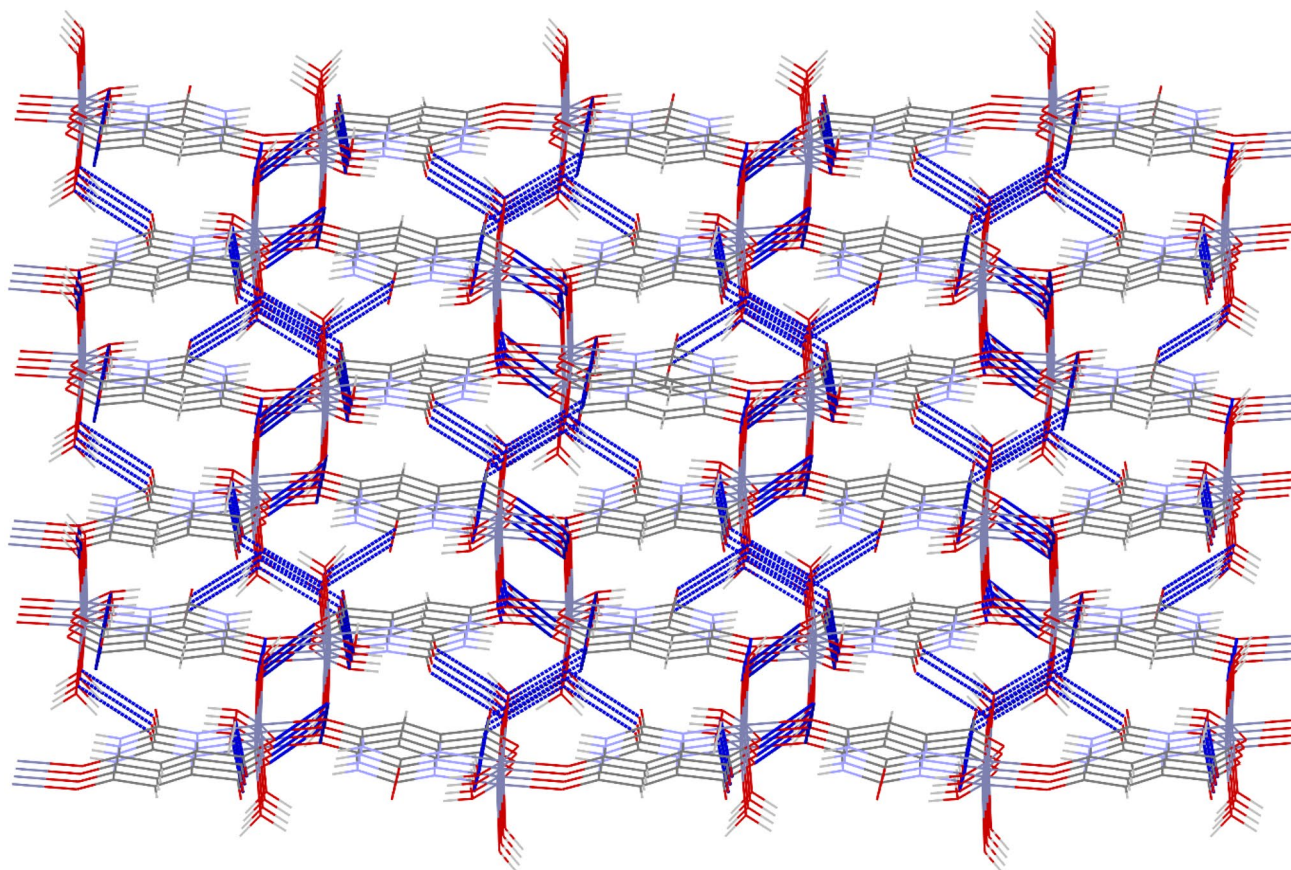


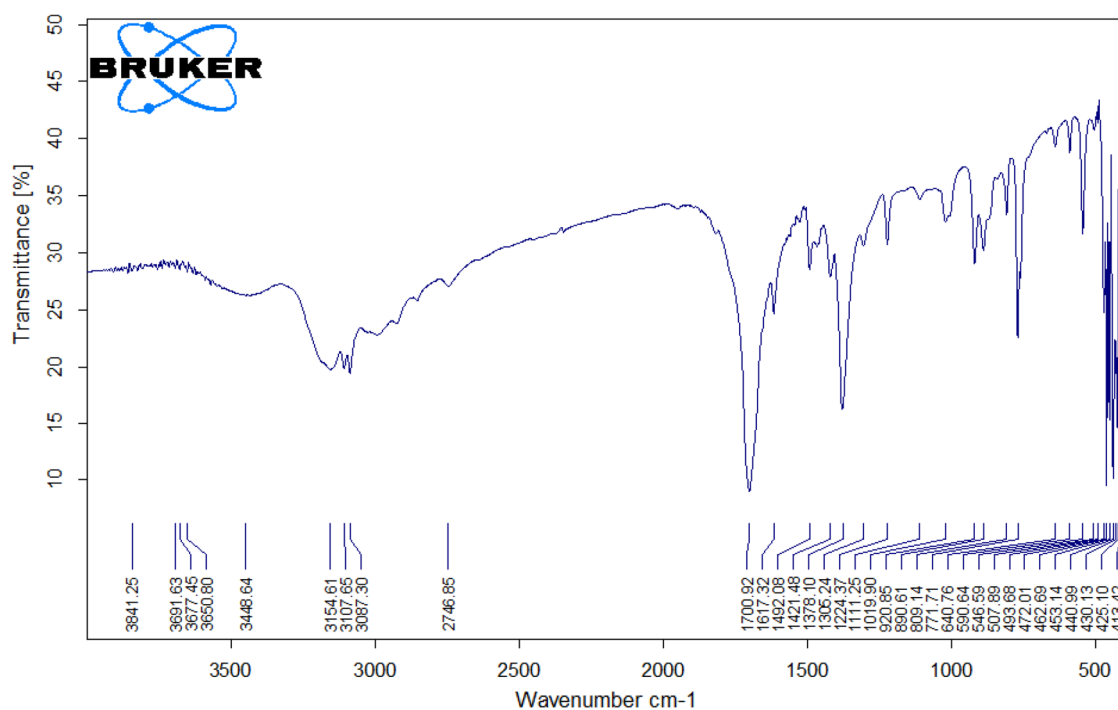
Fig. 6 Side view of crystal structure in **1** down to crystallographically “*b*” axis showing elevation of 1D coordination polymer into 3D hydrogen bonded network

3.4 Luminescence properties of $[\text{Zn}(\text{HOR})\cdot 3\text{H}_2\text{O}]_n$ (**1**)

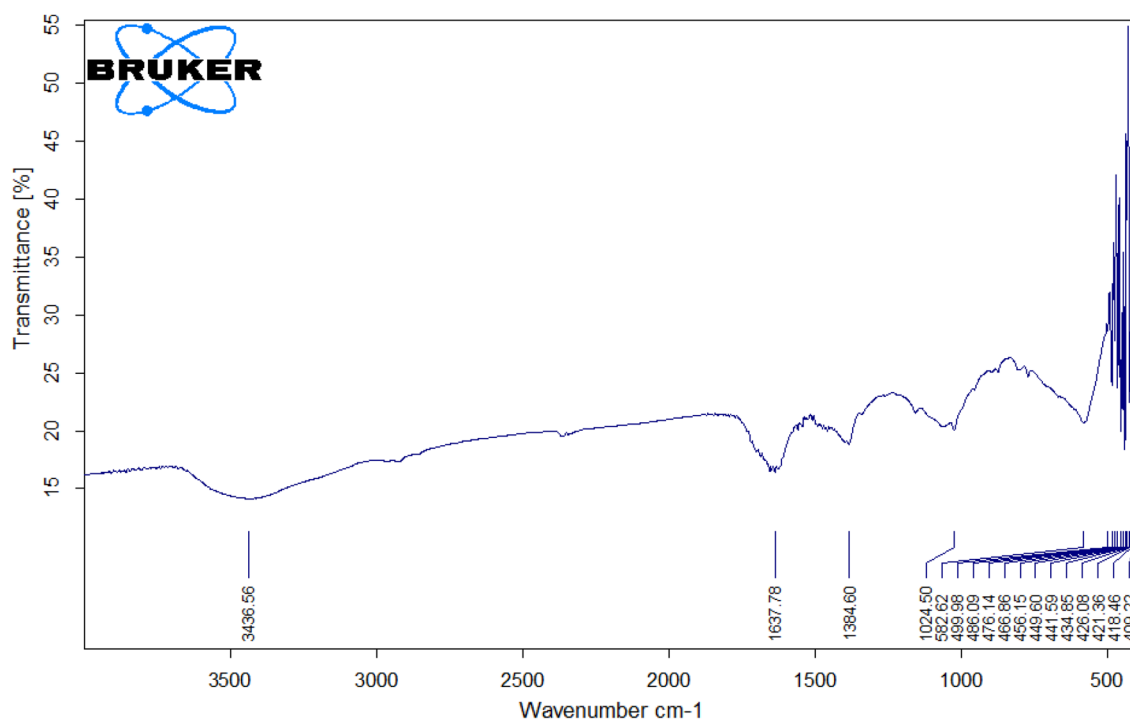
Coordination polymers have been identified to enact convenient characteristics with d^{10} electronic configuration because of their huger strength and the capacity of modulating transmission wavelength of organic crystalline material on coordination.

The solid state photoluminescence properties accomplishment of **1** and free ligands were inspected at room temperature (Fig. 10). Excitation at 270 nm and 290 nm cause fluorescent with emission maximal around 376 nm (3.2975 eV) and 362 nm (3.4250 eV) for Zn-*orotate* coordination polymer (**1**) and ligand (**K(H₂Or**)) respectively.

Because of the solidity enhancement of ligand in the complex the fluorescent intensity of **1** is greater than the free ligand. These type of fluorescent performances are carried by an intra ligand ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions) emission condition that causes the broad emission band of **1** and is having same patterns as in described Zn(II) or metal complexes with O and N-donor ligands having d^{10} configuration [41–46]. The resemblance among free ligand and emission spectra of complex eradicate the emission intensity, leads to show, luminescent property of the complex which is HOR^{-2} plated emission. Red shift of 12–14 nm has been shown by the free ligand in **1** which arise from the metal atom to ligand coordination. The HOMO–LUMO

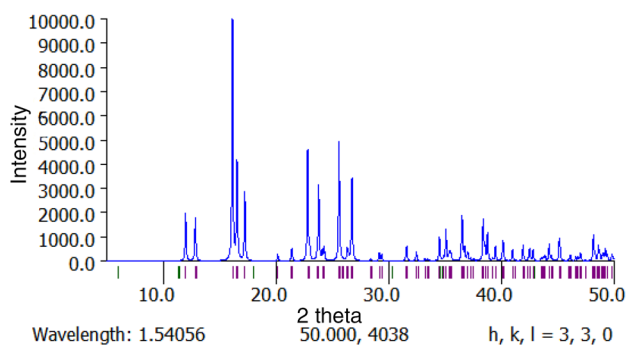


(a)

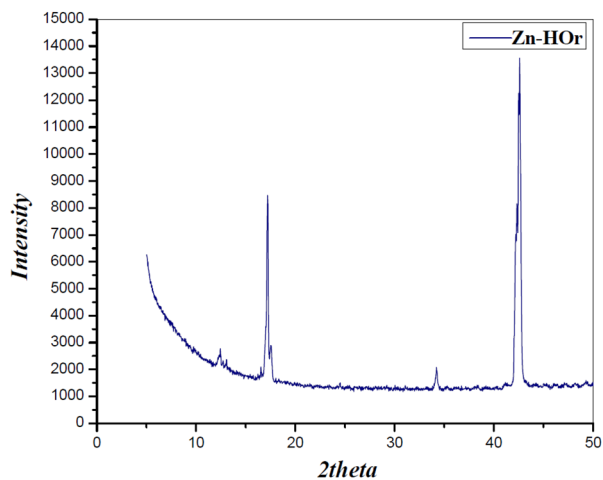


(b)

Fig. 7 The Fourier transform infrared (FTIR) spectra of K(H₂Or) (a), Zn-oroate (b)



(a)



(b)

Fig. 8 PXRD patterns of simulated (a), as-synthesized complex **1** (b)

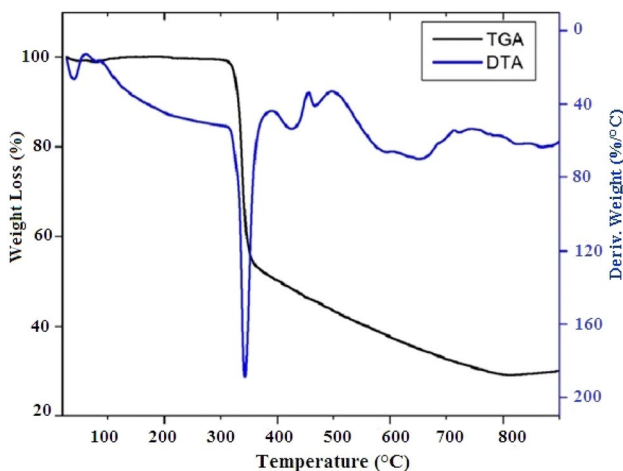


Fig. 9 TGA/DTA plot for **1**

Scheme 2 Thermal decomposition of **1**

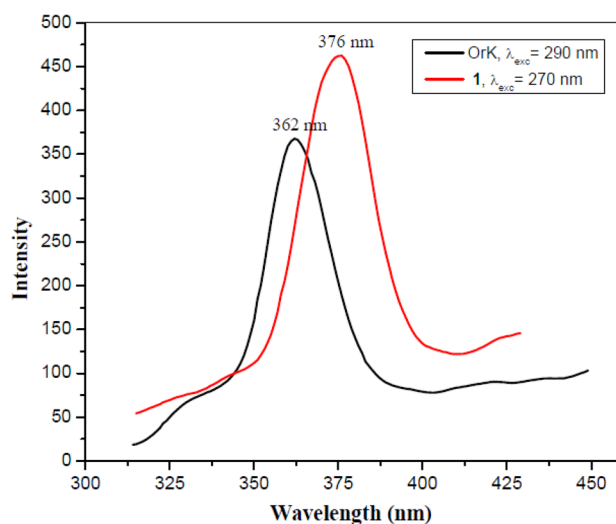
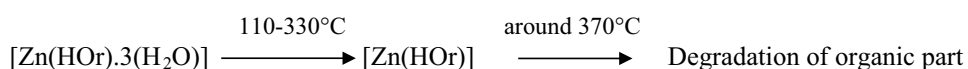


Fig. 10 Luminescence emission spectra of Zn-orotate complex and free ligand in solid. The excitation wavelength (λ_{exc}) is 270 nm for **1** (red color) and 290 nm for free ligand of $\text{K}(\text{H}_2\text{Or})$ (black color)

energy gap of the complex [47–53] decreases because of the red shift of emission energy of the ligand to the complex perhaps associated to the coordination of $\text{K}(\text{H}_2\text{Or})$ ligand to $\text{Zn}(\text{II})$ ions. The strengthening of $\text{Zn}(\text{II})$ productively, enhances the conformational toughness of ligand along with lowers loss of energy via vibrational motions. The reinforce fluorescence intensity of **1** is resolved. Emission behavior of the coordination polymer and free ligand shows an ideal photoactive material, associated with the certainty that **1** has higher thermal constancy and nearly insoluble in organic solvents for instance, acetone, benzene, chloroform, methanol and water.

4 Conclusion

We have reported Zn-orotate coordination polymer based on a ligand (pyrimidyl carboxylic acid or orotic acid potassium salt) having both metal coordination sites and peripheral hydrogen bonding groups that occurs after complex formation and are observed to play major role towards the self-assembly of 2D coordination network in **1**. The levitation of dimensionalities (3D) in the coordination polymers are induced by the hydrogen bonding involving $\text{O}-\text{H}\cdots\text{O}$ synthons in **1**. With high thermal stability and with peak maximal of 376 nm (3.2975 eV) Zn-orotate might be useful as photovoltaic material.

5 Supporting information available

X-ray crystallographic files in CIF format for the structures reported in this paper have been deposited to the Cambridge Crystallographic Data Center. CCDC Number for 1 is 1960035. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: C44 1223 336033; Email: deposit@ccdc.cam.ac.uk; Web: <http://www.ccdc.cam.ac.uk/deposit>].

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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