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A thermally labile copper (II) complex with hetero *N*- and *O*-donor ligands: Crystal structure, Hirshfeld surfaces, thermal and luminescent properties

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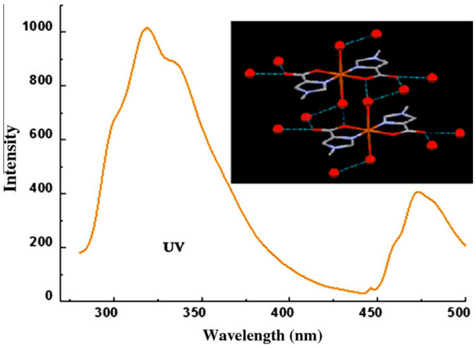
HIGHLIGHTS

- A new copper (II) complex with hetero *N*- and *O*-donor ligands has been prepared.
- The coordinated water molecules play a key role in the construction of crystal structures.
- The intermolecular interactions and solid state luminescent properties have been investigated.

GRAPHICAL ABSTRACT



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ABSTRACT

A new complex ($[Cu(\boldsymbol{L_1})_2(H_2O)_2]\cdot 2H_2O$, 1) derived from a hetero N- and O-donor ligand 5-methyl-imidazole-3-carboxylic acid ($\boldsymbol{L_1}$H) has been synthesized and characterized. Comparisons between $[Cu(\boldsymbol{L_1})_2(H_2O)_2]\cdot 2H_2O$, $[Co(\boldsymbol{L_2})(H_2O)]_2\cdot H_2O$ (**2**), and $[Cu(\boldsymbol{L_2})_2H_2O]\cdot H_2O$ ($\boldsymbol{L_2}$H = 5-methyl-isoxazole-3-carboxylic acid) revealed that the coordinated water molecules play a key role in the construction of crystal structures: two coordinated water molecules in the axial positions lead to single-deck 1D chain and 3D motif while one coordinated water molecule resulted to double-deck 1D chain and 2D stacking motif. Molecular Hirshfeld surfaces revealed that complexes **1** and **2** were supported mainly by H–H, C–H···π, and O–H···O intermolecular interactions. The room temperature solid state luminescent properties of complexes **1** and **2** were all shown as two distinct bands, which attribute to ligand–metal charge transfer and metal purterbed ligand centered emission.

Introduction

In recent years, considerable attentions have been paid to the construction of metal – organic frameworks (MOFs) by using multidentate N- and O-donor ligands in the field of coordinate chemistry and crystal engineering, for their topological diversities and potential application in medical chemistry (chemotherapeutic agents, anticancer drugs, antibiotic drugs, and so on) and functional materials (gas storage, luminescence, magnetism, sensor technology, catalysis, non liner optics, and so on) [1–8]. Multidentate N- and O-donor ligands usually act as organic spacers for the multidimensional frameworks and display various physical and chemical properties [9–13].

The prediction and computation of molecular crystal structure through the aspect of intermolecular interactions through Hirshfeld surfaces also have attracted attention in recently years [14–16]. Hirshfeld surfaces serves as a powerful tool for elucidating molecular crystal structure, it is a space partitioning construct that summarises the crystal packing into a single 3D surface, and

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the 3D surface can reduced into a 2D fingerprint plot, which summarise the complex information on intermolecular interactions present in crystals [15]. The principles of Hirshfeld surface and fingerprint plot were reported in other literature [14].

To obtain novel *N*- and *O*-donor ligand complexes with interesting architecture and properties, we focused on the investigation of the complexation of new *N*- and *O*-donor ligand 5-methyl -imidazole-3-carboxylic acid ($\boldsymbol{L}_1$H) and 5-methyl-isoxazole -3-carboxylic acid ($\boldsymbol{L}_2$H) (Scheme 1) with transition metals. $\boldsymbol{L}_1$H and $\boldsymbol{L}_2$H are occupied important positions in medical chemistry duo to the significant biological activity [17,18]. Additionally, the existence of carboxylic acid moiety and the nitrogen atom make them excellent multidentate ligands for coordination chemistry. Hitherto, no coordination compounds with $\boldsymbol{L}_1$H are known and only one copper (II) complex with $\boldsymbol{L}_2$H ([Cu (5-methyl-isoxazole-3-carboxylato)$_2$ (H_2O)$_2$]) has been reported by Birk and co-authors [19]. In our previous work [20], we reported the synthesis and crystal structure of a cobalt (II) complex with $\boldsymbol{L}_2$H ([Co($\boldsymbol{L}_2$)$_2$(H_2O]$_2$]·H_2O). As part of our systematic studies on N- and O-donor ligand systems, here we report the synthesis, crystal structure, thermal and luminescent properties of copper (II) complex with $\boldsymbol{L}_1$H (**1**, [Cu($\boldsymbol{L}_1$)$_2$ (H_2O]$_2$] 2H_2O), as well as thermal and luminescent properties of the reported cobalt (II) complex with $\boldsymbol{L}_2$H (**2**, [Co($\boldsymbol{L}_2$)$_2$(H_2O]$_2$] H_2O). We further compared the crystal structures of complexes **1** and **2** by using Hirshfeld surfaces analysis.

Results and discussion

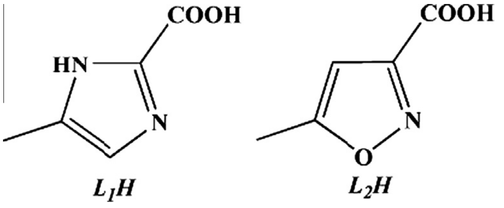
Crystal structure

The molecular structure of complex **1** was shown in Fig. 1. The selected bond lengths and bond angles were given in Table 1.

Complex **1** crystallizes as blue block crystals in the monoclinic *P*2(*1*) space group with *Z* = 2, the asymmetric unit (ASU) consists of a mononuclear copper complex which completed by one Cu^{II} ion, two $\boldsymbol{L}_1$ ligands, two coordination water molecules and two lattice water molecules (Fig. 1). The coordination polyhedron around the six coordinated central Cu^{II} ion is formed by two equatorial $\boldsymbol{L}_1$ ligands in an O, N-bidentate fashion through the imidazolic donor nitrogen and the carboxylic oxygen ligator (average bond length Cu–N 1.9595 (2) Å, Cu–O 2.0065 (3) Å) and trans axial positions were occupied by two lattice water ligands (average bond length Cu–O 2.477 (2) Å).

The coordination polyhedron was described as an octahedron with Cu^{II} ion located on a crystallographic inversion centre. The O2W–Cu1–O1W bond angle is 177.51 (10)°, which is almost perpendicular to the equatorial basal plane with the angles between equatorial and axial ligands were found to be O1W–Cu1–O1: 89.88(6)°, O1W–Cu1–N1: 92.28(10)°, O1W–Cu1–O3: 90.90(6)°, O1W–Cu1–N3: 89.13(6)°. The angles between the two equatorial ligands were found to be N1–Cu1–O1: 82.28 (6)°, O1–Cu1–N3: 97.26 (6)°, N3–Cu1–O3: 83.20 (6)° and O3–Cu1–N1: 97.25 (6)° (Table 1).

The crystal structure of **1** was stabilized by two strong intermolecular O2W–H···O3 W (distance of 2.849 Å) and O4W–H···O2 (distance of 2.828 Å) hydrogen bonds interactions (Table 2). The different mononuclear copper complexes paralleled with each other along *a* axis into 1D chain structure through O–H···O hydrogen bonds and slight π···π interactions with planes separation of 5.324 Å (Fig. 2). The different 1D chain structures then connect with each other through intricate O–H···O hydrogen bonds interactions into 3D structure. Where, every 1D chain connects to four others mediated by the double donor and acceptors behaviour of the lattice water molecules (Fig. 3).



Scheme 1. Molecular structures of hetero ligands $\boldsymbol{L}_1$*H* and $\boldsymbol{L}_2$*H*.

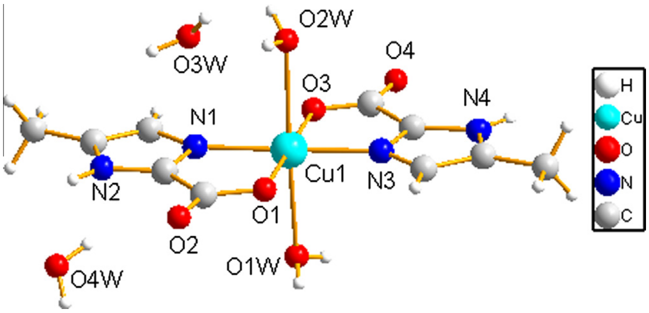


Fig. 1. Molecular structures of complex **1**.

For complex **2** [20], the ASU unit, the coordination polyhedron around cobalt (II), the 1D as well as 3D stacking motifs are all identical with **1** (Supporting information, Figs. S1 and S2). The bond angle for trans axis was 180.00 (6)° (Table S1), which is more close to standard octahedron than **1**. The planes separation for the 1D chain was 5.260 Å, the distances is a bit closer than that in **1** (Fig. S2).

While for the copper (II) complex with $\boldsymbol{L}_2$H ([Cu(5-methyl-isoxazole-3-carboxylato)$_2$(H_2O)$_2$]), the coordination polyhedron around centre copper (II) ion was five-coordinated pyramid geometry, with the equatorial basal plane are formed by two equatorial 5-methylisoxazole-3-carboxylates in an *O*, *N*-bidentate fashion and the axial position was occupied by one water molecules. The primary structure of it was the double-deck 1D chain connected by un-coordinated water molecules, then the adjacent double-deck 1D chains stacked into 2D motif inlayed (Fig. S4). Comparisons between complexes **1**, **2**, and [Cu(5-methyl-isoxazole-3-carboxylato)$_2$(H_2O)$_2$] revealed that the number of coordinated water molecules play a key role in the formation of these metal complexes with *N*- and *O*-donor ligands: two coordinated water molecules in the axial positions lead to single-deck 1D chain and 3D motif, while one coordinated water molecule resulted to double-deck 1D chain and 2D stacking motif.

Luminescent properties

The solid state luminescent properties of complexes **1** and **2** have been performed at room temperature. The emission spectra of them were shown in Fig. 5. These two complexes were all showed two distinct emission bands. Complex **1** shown emission maxima at 320 and 470 nm when excited at 280 nm, while complex **2** shown emission maxima at 360 and 440 nm when excited at 320 nm. Where, the bands at higher wave length were attributed to ligand–metal charge transfer, while the blue shifted bands were due to metal purterbed ligand centered emission bands [21].

Molecular Hirshfeld surfaces

3D d_{norm} surface is used for identification of very close intermolecular interactions. The value of d_{norm} is negative or positive when intermolecular contacts are shorter or longer than r^{vdW} (van der Waals (vdW) radii), respectively. The d_{norm} values are mapped onto the Hirshfeld surface by using a red–blue–white colour scheme: