



# A novel 4<sup>4</sup>.6<sup>6</sup> 5-connected metal-organic framework with strong fluorescent emission constructed by *m*-thioacetatebenzoic acid

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## ABSTRACT

A novel uninodal 5-connected metal-organic framework (MOF),  $[\text{Cd}_2\text{L}_2(4,4'\text{-bipy})_{3/2}(\text{H}_2\text{O})_2]_n$  ( $\text{H}_2\text{L} = m$ -thioacetatebenzoic acid and  $4,4'\text{-bipy} = 4,4'$ -bipyridine), was prepared under hydrothermal condition. It features an unusual brick-wall shape layer by  $4,4'$ -bipy, which consists of right- and left-handed helical chains arrayed alternatively and finally expands by  $\text{L}^{2-}$  to a rare 5-connected nov  $(4^4.6^6)$  topology network. Photoluminescence study reveals that it displays intense structure-related fluorescent emission bands ( $\lambda_{\text{ex}} = 355 \text{ nm}$ ) at 450 nm in the solid state at room temperature.

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## 1. Introduction

In recent years, extensive attention has been focused on the design and synthesis of zinc(II)/cadmium(II) carboxylate metal-organic frameworks (MOFs) for their various geometry chemistry of motifs, photoluminescent properties and other potential applications in molecular-based materials [1–4]. So far, a wide range of one- or multi-dimensional infinite solid-state coordination architectures have been achieved in the last decade [5–17], especially aromatic multibenzene-carboxylate ligands together with neutral N-based ligands such as  $4,4'$ -bipy has been extensively employed in the construction of mixed-ligand MOFs [18–20]. However, the coordination chemistry and structural properties of Cd(II) MOFs based on thioacetatebenzoic acid ligand have been documented very little to date. The thioacetatebenzoic acid ligand includes two different carboxylate systems. The characteristic coordination chemistry of the rigid carboxylate system may facilitate the formation of inorganic–organic materials with high thermal stability and form large channels, while the peculiar coordination chemistry of the flexible carboxylate system employed in the self-assembly reaction has versatile coordination behavior and may be favorable for the formation of the helical structure. What is more, it contains sulfur atom which can also take part in coordination, so it has five potential binding sites when coordinating to a metal center. In addition,  $4,4'$ -bipy has

been attracted considerable interests for the formation of extended structures by bridging metal nodes and is very important for the preparation of open frameworks with dimensionalities [21–23]. On the other hand, the  $d^{10}$  metals, especially Cd(II) ions, have been extensively used as functional metal centers because of luminescent characteristics arising from  $4d$  electrons [24–26].

Lately, the most usual and efficient strategy for synthesizing MOFs is based on a “building block” approach, and the topology of the final structure is greatly dependent on the geometry of the nodes (connection centers) and/or the flexibility of the “building blocks”. Among these networks, 3-, 4- and 6-connected MOFs are commonly observed [27–30], 5-, 7-, and 8-connected MOFs remain relatively scarce. According to the design strategy, we have synthesized a new 5-connected luminescent MOF,  $[\text{Cd}_2\text{L}_2(4,4'\text{-bipy})_{3/2}(\text{H}_2\text{O})_2]_n$ .

## 2. Experiment section

### 2.1. Materials and measurements

The ligand of *m*-thioacetatebenzoic acid ( $\text{H}_2\text{L}$ ) was prepared according to the method of literature [31]. All other reagents were purchased commercially and used as supplied. Hydrothermal reactions were performed in the 25 mL Teflon-lined stainless-steel Parr bomb. Data collection was performed with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Bruker APEX II area-detector diffractometer. Elemental analyses were carried out using a Perkin-Elmer 2400 II

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elemental analyzer. The excitation and luminescence spectra were performed on a HITACHIF-2500 fluorescence spectrometer in solid state at room temperature.

## 2.2. Synthesis of $[Cd_2L_2(4,4'-bipy)_{3/2}(H_2O)_2]_n$

$Cd(CH_3COO)_2 \cdot 2H_2O$  (1.0 mmol, 0.267 g),  $H_2L$  (1.0 mmol, 0.212 g), and 4,4'-bipy (0.2 mmol, 0.0396 g) were mixed in 15 mL distilled water. Then the mixture was transferred into a Parr Teflon-lined stainless-steel vessel (25 mL) and heated to 160 °C for 72 h. It was cooled to room temperature over 3 d. Colorless crystals were obtained and collected by filtration, washed with water, then dried in air, 81% yield (based on  $H_2L$ ). Anal. Calcd. (%) for  $C_{33}H_{28}Cd_2N_3O_{10}S_2$ : C, 43.14; H, 3.07; N, 4.58; S, 6.97. Found: C, 43.11; H, 3.02; N, 4.61; S, 6.95.

## 2.3. Single-crystal structure determination

The diffraction data was collected on a Bruker APXE II diffractometer equipped with a graphite-monochromatized  $MoK\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) up to a  $2\theta$  limit of  $55.0^\circ$  at 296(2) K. Data intensity was corrected by Lorentz-polarization factors and

**Table 1**  
Crystal data and structure refinement.

Empirical formula	$C_{33}H_{28}Cd_2N_3O_{10}S_2$
Formula weight	915.50
Crystal system	Monoclinic
Space group	$P2_1/n$
$a$ (Å)	11.4510(1)
$b$ (Å)	18.3188(2)
$c$ (Å)	16.2454(2)
$\beta$ (°)	104.080(1)
$V$ (Å <sup>3</sup> )	3305.40(6)
$Z$	4
$D_c$ (mg/m <sup>3</sup> )	1.840
$\mu$ (mm <sup>-1</sup> )	1.477
$F(000)$	1820
$\theta$ range	1.70–27.43
Reflections collected, unique, $R_{int}$	28760, 7523, 0.0301
Reflections observed [ $I > 2\sigma(I)$ ]	6363
Parameters refined	463
Goodness-of-fit on $F^2$	1.033
$R/wR$ [ $I > 2\sigma(I)$ ]	0.0255, 0.0545
$R/wR$ (all data)	0.0338, 0.0578
Max., Min. $\Delta\rho$ (eÅ <sup>-3</sup> )	0.342, -0.406

**Table 2**  
Selected bond distances (Å) and bond angles (°).

Cd(1)–O(7)	2.2697(16)	Cd(1)–N(1)	2.3266(18)	Cd(1)–N(3)#2	2.388(2)
Cd(1)–O(2W)	2.2854(17)	Cd(1)–O(3)#1	2.3390(17)	Cd(1)–O(4)#1	2.4041(18)
Cd(2)–O(1)	2.2616(17)	Cd(2)–O(1W)	2.3743(19)	Cd(2)–O(5)#3	2.3353(18)
Cd(2)–N(2)	2.3032(19)	Cd(2)–O(8)	2.3905(16)	Cd(2)–O(6)#3	2.5253(16)
Cd(2)–S(2)	2.9984(6)	O(3)#1–Cd(1)–O(4)#1	54.90(6)	N(1)–Cd(1)–O(4)#1	89.65(7)
O(7)–Cd(1)–O(2W)	86.79(7)	N(3)#2–Cd(1)–O(4)#1	151.77(6)	O(1)–Cd(2)–O(6)#3	86.57(6)
O(7)–Cd(1)–N(1)	88.86(6)	O(1)–Cd(2)–N(2)	166.41(7)	N(2)–Cd(2)–O(6)#3	106.47(7)
O(2W)–Cd(1)–N(1)	175.19(7)	O(1)–Cd(2)–O(5)#3	93.16(7)	O(5)#3–Cd(2)–O(6)#3	53.38(6)
O(7)–Cd(1)–O(3)#1	170.36(6)	N(2)–Cd(2)–O(5)#3	91.72(7)	O(1W)–Cd(2)–O(6)#3	80.38(6)
O(2W)–Cd(1)–O(3)#1	83.86(7)	O(1)–Cd(2)–O(1W)	98.01(7)	O(8)–Cd(2)–O(6)#3	155.01(5)
N(1)–Cd(1)–O(3)#1	100.40(7)	N(2)–Cd(2)–O(1W)	88.16(7)	O(1)–Cd(2)–S(2)	85.27(5)
O(7)–Cd(1)–N(3)#2	85.11(6)	O(5)#3–Cd(2)–O(1W)	131.59(6)	N(2)–Cd(2)–S(2)	82.99(5)
O(2W)–Cd(1)–N(3)#2	89.70(8)	O(1)–Cd(2)–O(8)	82.24(6)	O(5)#3–Cd(2)–S(2)	80.99(4)
N(1)–Cd(1)–N(3)#2	91.98(7)	N(2)–Cd(2)–O(8)	87.08(6)	O(1W)–Cd(2)–S(2)	146.61(5)
O(3)#1–Cd(1)–N(3)#2	97.17(6)	O(5)#3–Cd(2)–O(8)	149.20(6)	O(8)–Cd(2)–S(2)	68.32(4)
O(7)–Cd(1)–O(4)#1	123.10(6)	O(1W)–Cd(2)–O(8)	79.16(6)	O(6)#3–Cd(2)–S(2)	133.00(4)
O(2W)–Cd(1)–O(4)#1	91.00(8)				

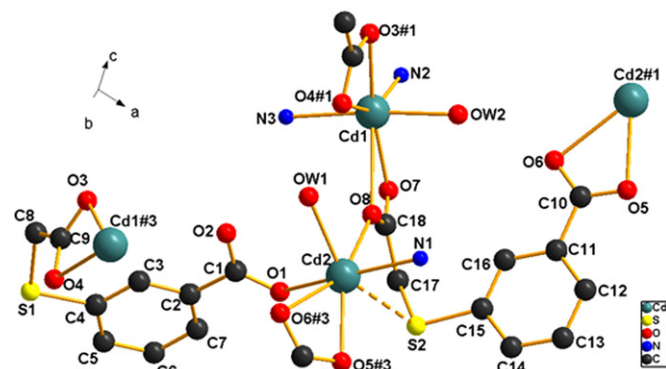
Symmetry codes: #1  $x+1/2, -y+1/2, z+1/2$ ; #2  $-x+3/2, y+1/2, -z+3/2$ ; #3  $x-1/2, -y+1/2, z-1/2$ .

empirical absorption. The structure was solved by direct methods and expanded with difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Except the hydrogen atoms on oxygen atoms were located in successive difference Fourier syntheses, the other hydrogen atoms were generated geometrically. All calculations were performed with SHELXTL-97 package [32]. The crystal data and structure refinement are summarized in Table 1, and the selected bond lengths and bond angles are listed in Table 2.

## 3. Results and discussion

### 3.1. Crystal structure

A single-crystal X-ray diffraction study reveals that the title compound is a unique three-dimensional (3D) open framework consisting of two crystallographically independent Cd(II), two individual  $L^{2-}$  ligands, one and half distinct 4,4'-bipy and two water molecules, as shown in Fig. 1. Cd(1) is coordinated to four oxygen atoms from flexible carboxylic groups of two individual  $L^{2-}$  ligands (Cd–O 2.2697(16)–2.4041(18) Å), two N atoms belonging to different 4,4'-bipy (Cd–N 2.3266(18) and 2.388(2) Å) and one water molecule (Cd–O 2.2854(17) Å) in a slightly distorted pentagonal-bipyramidal geometry. Cd(2) is coordinated to three oxygen atoms from rigid carboxylic groups of two individual  $L^{2-}$  ligands, one oxygen atom from flexible carboxylic group (Cd–O 2.2616(17)–2.5253(16) Å), one N atom of 4,4'-bipy (Cd–N 2.3032(19) Å) and one water



**Fig. 1.** Ball-and-stick representation (symmetry codes: #1  $x+1/2, -y+1/2, z+1/2$ ; #2  $-x+3/2, y+1/2, -z+3/2$ ; #3  $x-1/2, -y+1/2, z-1/2$ ).

molecule (Cd–O 2.3743(19)Å) in distorted octahedron geometry. The bridging Cd(1)–O(8)–Cd(2) angle of 150.63(7)° is in the range of reported complexes [33] and the Cd(1)⋯Cd(2) separation is 5.054(2)Å. It is worthwhile to note that the Cd(2)⋯S(2) distance of 2.9984(6)Å suggests the non-negligible interaction between Cd(2) and S(2), which may be described as a semichelating coordination mode [34]. Hence Cd(2) can also be regarded as a pseu-pentagonal-bipyramidal environment. The carboxylate groups of  $L^{2-}$  ligand are all deprotonated and coordinate to Cd(II) atoms in three different fashions: unidentate, chelate and  $\mu_2$ -chelate fashions. The two independent  $L^{2-}$  ligands bridge metal centers in a head-to-tail mode via formyl and acetic groups to form one-dimensional (1D) dichains consisting of 20-membered subrings (Fig. 2).

In Fig. 3, two kinds of 4,4'-bipy link metallic centers forming brick-wall shape structure on  $ab$  plane are shown. Two pyridine rings including N(1) atoms are coplane, while the dihedral angle between the pyridine ring including N(2) atom and the ring including N(3) atom is 56.68(8)°. What is more, there are alternately right- and left-handed helices with the pitch of 18.319(3)Å on the 2D layer, so the whole sheet does not show chirality (Fig. 3). It finally expands to 3D network by  $L^{2-}$  ligands.

Taking the structural feature into account in view point of topology for clarity, as depicted in Fig. 4, taking two Cd(II) atoms joined by O8 atom as a secondary building unit (SBU), such SBU connects three 4,4'-bipy and four  $L^{2-}$  ligands, but these  $L^{2-}$  ligands as edges connect two SBUs. So the SBU is only reduced into a 5-connected node. Topology analysis indicates it is a quite rare 5-connected nov net with a Schläfli symbol of  $(4^4.6^6)$ . The vertex symbol calculation using OLEX gives  $(4.4.4.4.6.6_5.6_5.6_3.6.6_5)$  for the 5-connected node. Structures containing 5-connected metal centers are very rare, and only several examples of frameworks with 3D 5-connected networks have been reported to date [35–38]. The net reported here is based on the square pyramidal nodes, and it is obviously different from heterobimetallic network

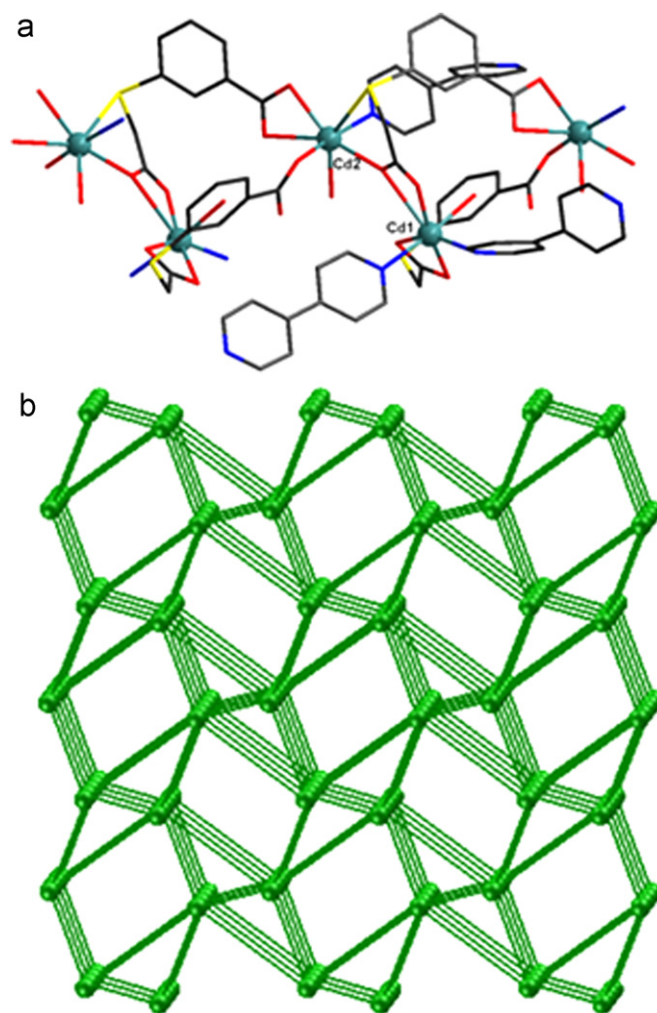


Fig. 3. 2D brick-wall shape structure on  $ab$  plane and its two different types of helical chains.

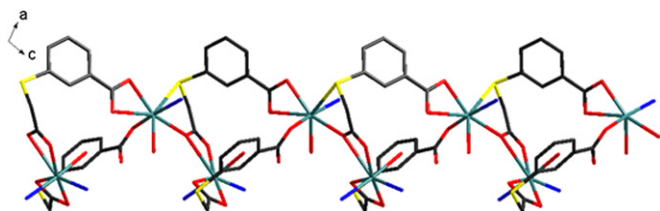


Fig. 2. 1D dichain down the  $b$ -axis.

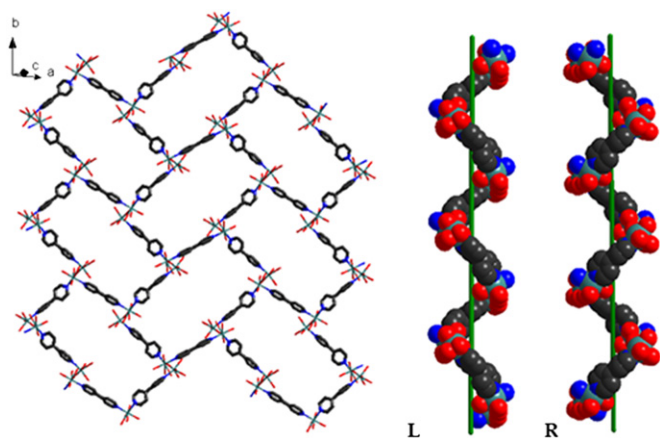


Fig. 4. Novel 5-connected nov  $(4^4.6^6)$  topology network.

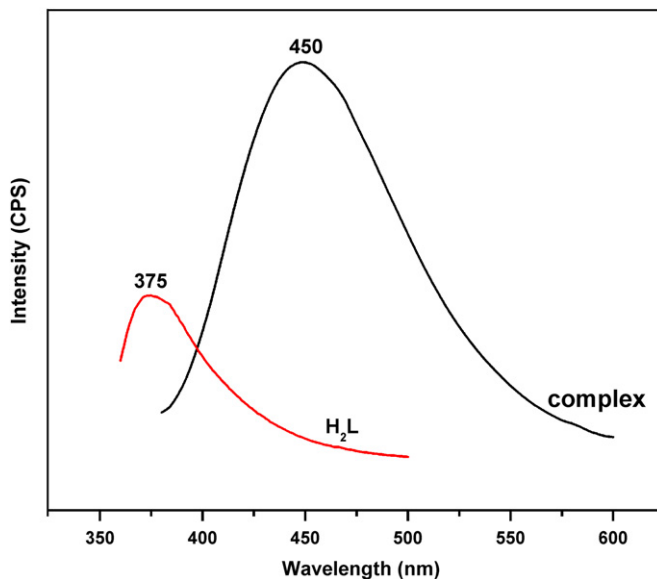


Fig. 5. Photoluminescent spectra of  $H_2L$  and its polymer in solid state at room temperature.

found in  $\text{Cu}(4,4'\text{-bipy})_{1.5}\text{Cr}_2\text{O}_7\text{H}_2\text{O}$  [39]. The stacking of the hexagonal layers is ABAB... in  $4^4.6^6$  nov topology network, which is different from the AAA... pattern in  $\text{Cu}(4,4'\text{-bipy})_{1.5}\text{Cr}_2\text{O}_7\text{H}_2\text{O}$  with  $4^6.6^4$  bnn topology network. As far as we know, the coordination polymer  $\{\text{Cu}_2(2,5\text{-Me}_2\text{pyz})[\text{N}(\text{CN})_2]_4\}_n$  ( $2,5\text{-Me}_2\text{pyz}=2,5\text{-dimethylpyrazine}$ ) is the only one reported as an example containing 5-connected metal centers with  $4^4.6^6$  topology [40].

### 3.2. Photoluminescent properties

The  $d^{10}$  metal compounds have been shown to exhibit some photoluminescent properties [41,42]. The solid-state luminescent properties of  $\text{H}_2\text{L}$  ligand and title polymer were investigated at

room temperature and their emission spectra are given in Fig. 5. For title polymer, its fluorescent emission spectrum exhibits an intense photoluminescence at 450 nm. In order to understand the nature of the emission bands of title polymer, we further measured the emission spectrum of the free  $\text{H}_2\text{L}$  ligand, which shows one peak emission at 375 nm. It is known that free  $4,4'\text{-bipy}$  ligand displays the fluorescent property with a maximum emission peak of 430 nm [43,44]. The maximum emission bands of title polymer are red-shifted compared to free  $\text{H}_2\text{L}$  ligand; therefore, the emission band of title polymer may be mainly assigned to ligand-to-metal charge transfer (LMCT) [45]. The coordination enhances the "rigidity" of the ligands and thus reduces the loss of energy through a radiationless pathway. Since the title polymer is colorless and insoluble in common polar and nonpolar solvents, it may be good candidates for potential photoactive materials (Figs. 6 and 7).

### 4. Conclusion

A new luminescent MOF,  $[\text{Cd}_2\text{L}_2(4,4'\text{-bipy})_{3/2}(\text{H}_2\text{O})_2]_n$ , has been synthesized and characterized. It features an unusual brick-wall shape layer by  $4,4'\text{-bipy}$ , which consists of right- and left-handed helical chains arrayed alternatively and finally expands by  $\text{L}^{2-}$  to 3D rare 5-connected nov ( $4^4.6^6$ ) topology network. Photoluminescence study shows that the MOF displays intense blue-green fluorescent emission bands.

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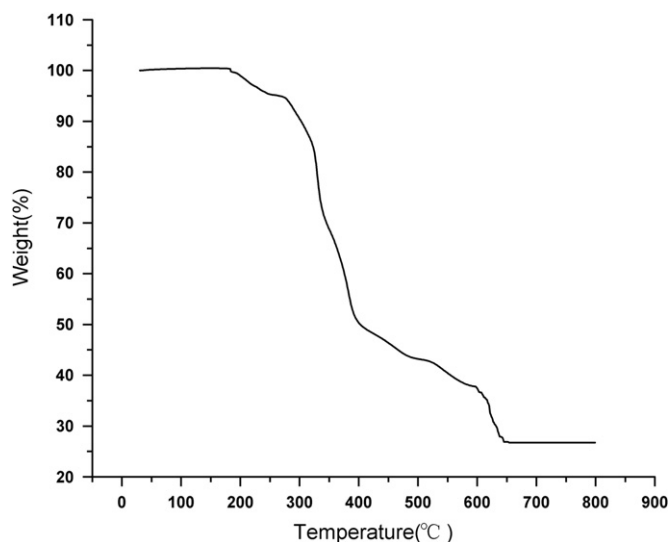


Fig. 6. The TG curves of 1.

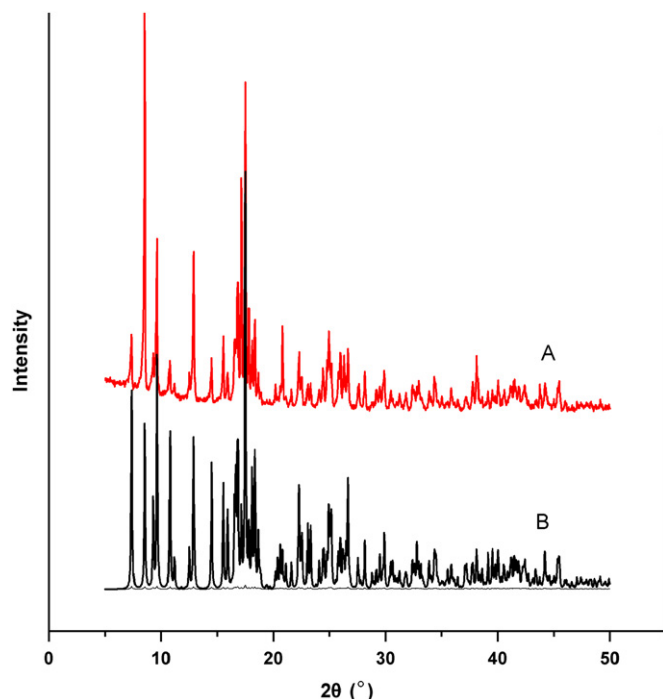


Fig. 7. Experimental (A) and simulated (B) XRPD spectra of title complex.

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