

Scientific paper

# Synthesis, Structure Evaluation, Spectroscopic and Antibacterial Investigation of Metal Complexes with 2-(Pyridin-4-yl)quinoline-4-carboxylic Acid

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Received: 07-09-2016

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## Abstract

Four metal complexes based on quinoline carboxylate ligand from 2-(pyridin-4-yl)quinoline-4-carboxylic acid (**HL**),  $\{[ML_2(H_2O)_2] \cdot 2H_2O\}_n$  ( $M = Mn^{II}$ , **1**;  $M = Co^{II}$ , **2**;  $M = Cd^{II}$ , **3**) and  $\{[Ag_2L_2(H_2O)_2] \cdot 3H_2O\}_n$  (**4**) have been synthesized under hydrothermal conditions. Their structures were determined by elemental analyses, IR spectra, and further characterized by single-crystal X-ray diffraction analysis. Complexes **1–3** feature a 1D chain structure which is further linked together to construct the 3D supramolecular network through hydrogen bonds. Complex **4** exhibits a 3D configuration. The fluorescent behavior and antibacterial activities of these compounds have been investigated.

**Keywords:** Quinoline derivative; X-ray crystal structure; fluorescent property; antibacterial activity

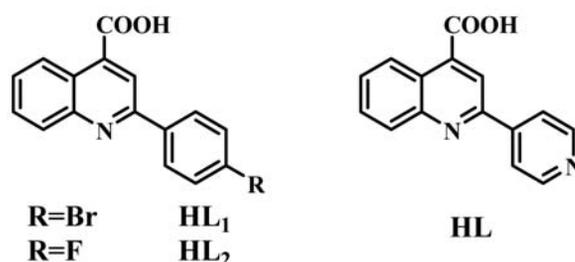
## 1. Introduction

Since Pt-based drugs play a significant role in anti-tumor chemotherapy, development of metal complexes possessing biological activities has been an active research field.<sup>1,2</sup> The biological properties of metal complexes depend on the organic ligands and the nature of metal ions. Thereby, the combination of suitable metal ion as well as ligand is an important prerequisite for the construction of bioactive metal complex.<sup>3,4</sup>

Quinoline scaffold has been known for wide spectrum of biological and pharmaceutical activities, such as antimalarial,<sup>5,6</sup> antitumor,<sup>7,8</sup> antibacterial,<sup>9,10</sup> and anti-allergic.<sup>11</sup> Carboxyl modified heterocycle compounds are also excellent metal-binding compounds, which exhibit versatile coordination modes depending on reaction conditions and the nature of central metal ion.<sup>12–14</sup>

In our earlier investigations, we have shown that dinuclear complexes of Mn(II), Co(II), Cd(II), and Zn(II) based on 2-phenylquinoline carboxylic derivatives **HL**<sub>1</sub> and **HL**<sub>2</sub> (Scheme 1) possess broad and effective antibacterial activity.<sup>14,15</sup> These results prompted us to examine

the controlling factors on the antibacterial activity of metal complex based on quinoline derivatives. In continuation of our work, this paper deals with the synthesis and characterization of four metal complexes,  $\{[ML_2(H_2O)_2] \cdot 2H_2O\}_n$  ( $M = Mn^{II}$ , **1**;  $M = Co^{II}$ , **2**;  $M = Cd^{II}$ , **3**) and  $\{[Ag_2L_2(H_2O)_2] \cdot 4H_2O\}_n$  (**4**), derived from 2-pyridylquinoline derivative 2-(pyridin-4-yl)quinoline-4-carboxylic acid (**HL**). The photoluminescent property and antibacterial assays over gram-positive and gram-negative bacterial strains are also presented in this manuscript.



Scheme 1. Structure of ligands **HL**<sub>1</sub>, **HL**<sub>2</sub> and **HL**.

## 2. Experimental Section

### 2. 1. Materials and Instruments

All the reactions were carried out under air atmosphere. All chemicals and solvents used in the synthesis were reagent grade without further purification.

The IR spectra were taken on a Vector22 Bruker spectrophotometer (400–4000  $\text{cm}^{-1}$ ) with KBr pellets. NMR spectra were measured on a Bruker AM 500 spectrometer. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer.

### 2. 2. Synthesis of 2-(Pyridin-4-yl)quinoline-4-carboxylic Acid (HL)

A mixture of isatin (1.18 g, 8.00 mmol), 4-acetylpyridine (0.24 g, 2.00 mmol), and potassium hydroxide (2.24 g, 40.00 mmol) in 2 mL of ethanol and 18 mL of water was mixed and refluxed for 10 hours. When the reaction was finished, the orange solution was cooled to room temperature and adjusted to pH 5 with 1 M HCl. The synthetic yellow precipitate was filtered, washed several times with water and dried. Yield: 1.16 g, 58%. IR (KBr,  $\text{cm}^{-1}$ ): 3431, 3064, 2759, 2445, 1942, 1720, 1609, 1588, 1541, 1500, 1456, 1416, 1348, 1308, 1253, 1152, 1060, 1016, 864, 835, 796, 778, 763, 735, 716, 652.  $^1\text{H-NMR}$  (500Hz, DMSO,  $\delta$ ): 8.79 (d,  $J = 5\text{Hz}$ , 2H), 8.67 (d,  $J = 10\text{Hz}$ , 1H), 8.46 (s, 1H), 8.25 (d,  $J = 10\text{Hz}$ , 2H), 8.19 (d,  $J = 10\text{Hz}$ , 1H), 7.87 (t, 1H), 7.73 (t, 1H). Anal. Calcd for  $\text{C}_{15}\text{H}_{10}\text{N}_2\text{O}_2$ : C, 71.99; H, 4.03; N, 11.19. Found: C, 72.21; H, 4.02; N, 11.22%.

### 2. 3. General Procedure for the Synthesis of Complexes 1–4

HL (0.10 mmol) and nitrates ( $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Co}(\text{NO}_3)_2$ ,  $\text{Cd}(\text{NO}_3)_2$ , or  $\text{AgNO}_3$ ) (0.10 mmol) in 10 mL mixed solvent of DMF/ $\text{CH}_3\text{OH}/\text{H}_2\text{O}$  ( $v/v/v = 2/4/4$ ) were sealed in 25 mL Teflon cup and heated at 90  $^\circ\text{C}$  for 2–3 days and cooled slowly to room temperature over a period of 20 h. Then crystals suitable for X-ray diffraction analysis were obtained.

$\{[\text{MnL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**1**) Yield: 0.026 g (42% on the basis of HL). IR (KBr,  $\text{cm}^{-1}$ ): 3214, 1608, 1581, 1501, 1421, 1396, 1327, 1308, 1239, 1067, 1013, 837, 813, 771, 655, 572, 546. Anal. Calcd. for  $\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_8\text{Mn}$ : C, 57.61; H, 4.19; N, 8.96. Found: C, 57.78; H, 4.18; N, 8.99%.

$\{[\text{CoL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**2**) Yield: 0.035 g (56% on the basis of HL). IR (KBr,  $\text{cm}^{-1}$ ): 3217, 1953, 1611, 1582, 1502, 1458, 1422, 1398, 1329, 1309, 1239, 1068, 1018, 870, 838, 814, 772, 721, 684, 572, 555. Anal. Calcd. for  $\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_8\text{Co}$ : C, 57.24; H, 4.16; N, 8.90. Found: C, 57.41; H, 4.15; N, 8.93%.

$\{[\text{CdL}_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**3**) Yield: 0.031 g (46% on the basis of HL). IR (KBr,  $\text{cm}^{-1}$ ): 3434, 3105, 1951, 1611,

1552, 1537, 1498, 1453, 1425, 1390, 1324, 1305, 1239, 1064, 1020, 866, 838, 804, 785, 660, 573. Anal. Calcd. for  $\text{C}_{30}\text{H}_{26}\text{N}_4\text{O}_8\text{Cd}$ : C, 52.76; H, 3.84; N, 8.20. Found: C, 52.92; H, 3.83; N, 8.22%.

$\{[\text{Ag}_2\text{L}_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\}_n$  (**4**) Yield: 0.035 g (43% on the basis of HL). IR (KBr,  $\text{cm}^{-1}$ ): 3401, 3080, 3036, 1948, 1599, 1574, 1492, 1455, 1417, 1380, 1321, 1152, 1066, 999, 864, 853, 814, 776, 720, 684, 571. Anal. Calcd. for  $\text{C}_{30}\text{H}_{29}\text{N}_4\text{O}_{10}\text{Ag}_2$ : C, 43.87; H, 3.56; N, 6.82. Found: C, 44.00; H, 3.55; N, 6.84%.

### 2. 4. X-Ray Data Collection and Structure Refinement

Structure measurements of all the complexes were performed on Bruker Smart Apex CCD diffractometer equipped with graphite-monochromated Mo  $K\alpha$  with radiation wavelength of 0.71073  $\text{Å}$  by using a  $\omega$ - $2\theta$  scan mode. The collected data were reduced using the SAINT program.<sup>16</sup> Absorption corrections were applied using SADABS program.<sup>17</sup> These structures were solved by direct methods and refined with the full-matrix least-squares technique using SHELXS-97.<sup>18</sup> Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The solvent molecules O8 and O9 in complex **4** were disordered over two positions (50: 50 occupancy). The hydrogen atoms bonded to C were generated geometrically; while the hydrogen atoms of the water molecules were located from difference maps and fixed at their ideal positions with O–H = 0.85(2)  $\text{Å}$ , H $\cdots$ H = 1.44(2)  $\text{Å}$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

### 2. 5. Bioassay Conditions

Four referenced bacterial strains, *B. subtilis*, *E. coli*, *P. aeruginosa* and *S. aureus* were selected. Streptomycin was used as a positive control. The  $\text{IC}_{50}$  (half minimum inhibitory concentrations) of the test compounds were determined by a colorimetric method using the dye MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium-bromide). Stock solutions of the synthesized compounds (100  $\mu\text{g}/\text{mL}$ ) were prepared in DMSO, and sequentially diluted with Mueller-Hinton medium. The antibacterial activities were evaluated by the method reported before.<sup>14,15,19</sup> The procedure of antimicrobial activity was given in detail in *Supporting Information*.

## 3. Results and Discussion

### 3. 1. Synthesis and General Characterization

Complexes **1–4** were constructed from HL and the related metal salt under hydrothermal conditions. All of complexes are soluble in high polarity solvents.

HL was prepared via the Pfitzinger reaction.<sup>14</sup> Characterization of the ligand has been accomplished by IR,  $^1\text{H NMR}$ , and elemental analysis. The FT-IR spectrum for

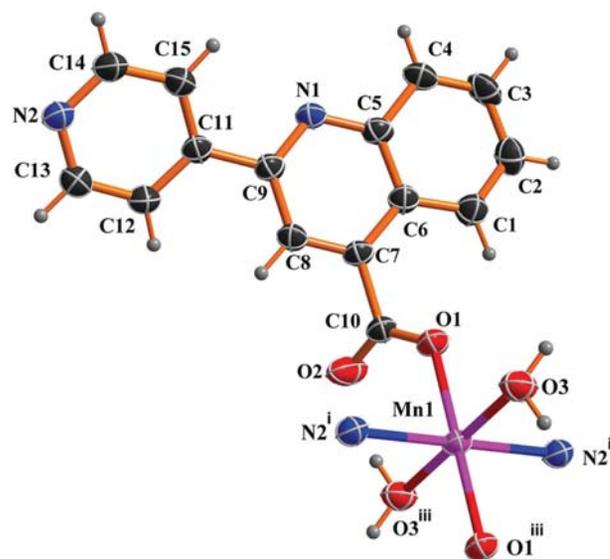
**Table 1.** Crystallographic data for 1–4.

|  | <b>1</b>               | <b>2</b>               | <b>3</b>               | <b>4</b>                 |
|--|------------------------|------------------------|------------------------|--------------------------|
| Empirical formula                            | $C_{30}H_{26}N_4O_8Mn$ | $C_{30}H_{26}N_4O_8Co$ | $C_{30}H_{26}N_4O_8Cd$ | $C_{30}H_{28}N_4O_9Ag_2$ |
| $M_r$  | 625.49                 | 629.48                 | 682.95                 | 804.30                   |
| Crystal system                               | triclinic              | triclinic              | triclinic              | monoclinic               |
| Space group                                  | $P\bar{1}$             | $P\bar{1}$             | $P\bar{1}$             | $Cc$                     |
| $a$ (Å)                                      | 8.5296(14)             | 8.5511(4)              | 8.6281(5)              | 14.2981(7)               |
| $b$ (Å)                                      | 8.8986(14)             | 8.7942(5)              | 8.9010(5)              | 17.5489(8)               |
| $c$ (Å)                                      | 10.5757(15)            | 10.4459(5)             | 10.6287(7)             | 13.4398(7)               |
| $\alpha$ (°)                                 | 71.300(4)              | 70.748(2)              | 72.133(2)              | 90.00                    |
| $\beta$ (°)                                  | 78.698(4)              | 78.9820(10)            | 78.500(2)              | 114.6570(10)             |
| $\gamma$ (°)                                 | 74.264(5)              | 74.252(2)              | 74.6320(10)            | 90.00                    |
| $V$ (Å <sup>3</sup> )                        | 726.59(19)             | 709.29(6)              | 742.90(8)              | 3064.8(3)                |
| $Z$  | 1                      | 1                      | 1                      | 4                        |
| $\rho_c$ (g cm <sup>-3</sup> )               | 1.429                  | 1.474                  | 1.527                  | 1.743                    |
| $F(000)$                                     | 323                    | 325                    | 346                    | 1608                     |
| $T$ / K                                      | 298(2)                 | 298(2)                 | 298(2)                 | 298(2)                   |
| $\mu$ (Mo-K $\alpha$ ) / mm <sup>1</sup>     | 0.512                  | 0.664                  | 0.791                  | 1.338                    |
| Data/param./restr.                           | 2748 / 196 / 0         | 2607 / 196 / 0         | 2877 / 196 / 0         | 6509 / 410 / 2           |
| GOF  | 1.023                  | 1.108                  | 1.131                  | 1.065                    |
| $R1, wR2$ ( $I > 2\sigma(I)$ )               | 0.0592 / 0.1414        | 0.0279 / 0.0720        | 0.0218 / 0.0561        | 0.0361 / 0.0913          |
| $R1, wR2$ (all data)                         | 0.0792 / 0.1543        | 0.0300 / 0.0733        | 0.0223 / 0.0569        | 0.0399 / 0.0939          |
| Large diff. peak / hole (e Å <sup>-3</sup> ) | 0.974 / -0.689         | 0.282 / -0.256         | 0.506 / -0.401         | 1.593 / -0.964           |

ligand **HL** shows characteristic C=O stretching vibration at 1720 cm<sup>-1</sup>. The absorption bands around 3400 cm<sup>-1</sup> corresponds to the presence of hydroxyl group. The infrared spectral peaks around 3064 cm<sup>-1</sup> are due to the aromatic C–H vibrations. The compounds **1–4** show similar types of vibration frequencies. An intense and broad band at about 3200 cm<sup>-1</sup> suggests the presence of water molecule. The  $\nu_{as}(\text{COO}^-)$  band is observed at around 1607 cm<sup>-1</sup>, while the  $\nu_s(\text{COO}^-)$  vibration is observed at about 1396 cm<sup>-1</sup>. The separation value  $\Delta\nu$  ( $\nu_{as}(\text{COO}^-) - \nu_s(\text{COO}^-)$ ) is about 211 cm<sup>-1</sup> which is in good agreement with the monodentate coordination mode features shown by the results of crystal structures.<sup>20</sup>

### 3. 2. Crystal Structures of Complexes 1–4

The solid structures of complexes **1–4** were determined by single-crystal X-ray diffraction. The crystallographic



**Figure 1.** The coordination environment of Mn(II) in **1** at 50% probability displacement. Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x, y + 1, z - 1$ ; (iii)  $-x + 1, -y + 2, -z$ .

**Table 2.** Selected Bond Distance (Å) and Angles (deg) for **1**.

|                          |          |  |          |
|--------------------------|----------|--|----------|
| Mn1–O1                   | 2.146(2) | Mn1–O3                                 | 2.173(2) |
| Mn1–N2 <sup>i</sup>      | 2.292(2) | O1–C10                                 | 1.240(3) |
| O2–C10                   | 1.239(4) |  |          |
| O1–Mn1–O1 <sup>iii</sup> | 180.0    | O1–Mn1–O3                              | 89.95(8) |
| O1–Mn1–O3 <sup>iii</sup> | 90.05(8) | O1–Mn1–N2 <sup>i</sup>                 | 88.40(8) |
| O1–Mn1–N2 <sup>ii</sup>  | 91.60(9) | O3 <sup>iii</sup> –Mn1–N2 <sup>i</sup> | 89.79(8) |
| O3–Mn1–N2 <sup>i</sup>   | 90.21(8) |  |          |

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ ; (ii)  $x, y + 1, z - 1$ ; (iii)  $-x + 1, -y + 2, -z$ .

and data collection parameters for complexes **1–4** are given in Table 1; selected bond lengths and angles are listed in Tables 2, 3 and S1, S2.

The result of single crystal analysis indicates that complexes **1–3** are isomorphous. They all crystallize in triclinic system, space group  $P\bar{1}$ , therefore, the crystal structure of **1** is described in detail herein as the example. The ORTEP plots of **1–3** are shown in Figures 1, S1 and S2.

There are half of the Mn(II) center, one deprotonated ligand  $L^{1-}$ , one coordinated water molecule, and one solvent water molecule in the asymmetric unit of **1**. As depicted in Fig. 1, the Mn(II) center is six-coordinated in pseudo-octahedral coordination geometry. The equatorial plane was defined by two coordination water molecules (O3 and O3<sup>iii</sup>), and two N atoms (N2<sup>i</sup> and N2<sup>ii</sup>) from two different pyridine rings. The axial positions are occupied by the monodentate carboxylic O atoms (O1 and O1<sup>iii</sup>). The sum of the equatorial bond angles are 360.0(8)°, which ensures the planarity of the equatorial plane. The axial O1–Mn1–O1<sup>iii</sup> bond angle of 180.0° clearly indicates the linear configuration. As shown in Table 2, the equatorial bond length distances between the Mn atom and the N, O atoms, 2.293(2) and 2.173(2) Å, are longer than the axial Mn1–O1 distance, 2.146(2) Å, showing the squashed octahedron configuration.

Compared with the metal complexes based on  $HL_1$  and  $HL_2$ ,<sup>14,15</sup>  $HL$  in **1** is more planar, as evidenced by the dihedral angle between the pyridine ring and the quinoline heterocycle being 21.01(1)°. The carboxylate group of  $HL$  in complex **1** adopts a monodentate coordination mode, while in previous reported dinuclear complex  $[Mn_2(L_1)_4(MeOH)_4]$ , the carboxylate group adopts a syn-syn bidentate coordination mode.<sup>14</sup>

As can be seen from Figure 2, the Mn(II) cations are bridged by the carboxylate and pyridine group to form a double chain structure extending along the crystallographic [0–1 1] direction with the nearest intrachain Mn...Mn distance of 11.431(2) Å. In complex **1**, the water molecules, acting as both hydrogen-donors and hydrogen-acceptor, play a crucial role in determining the supramolecular structure. First of all, the lattice water molecules are bonded to the chain *via* O4–H4A...O2, meanwhile the intrachain

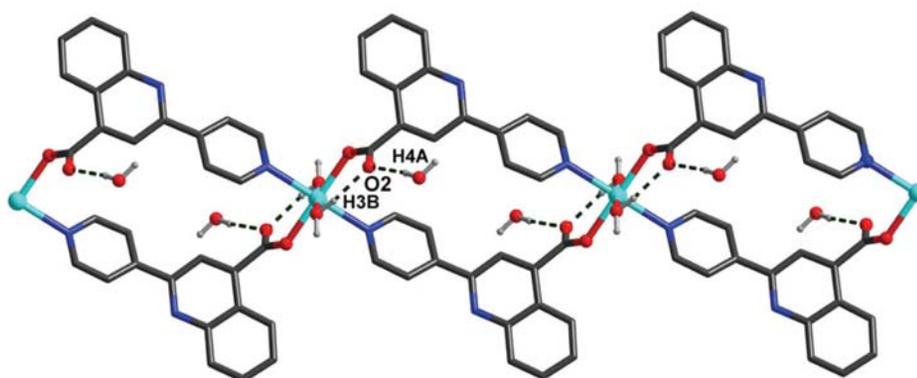


Figure 2. The one-dimensional double chain structure of **1**.

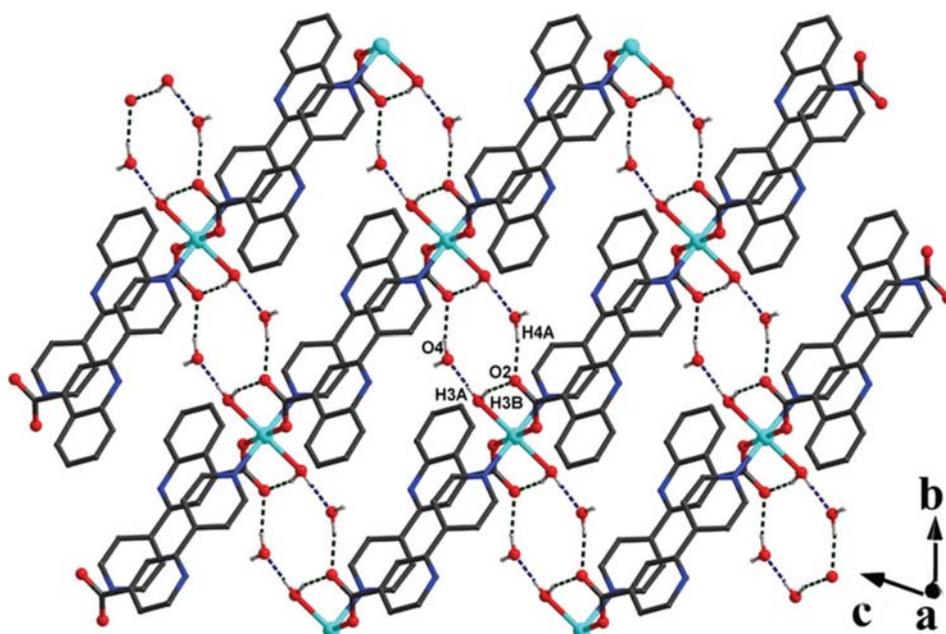


Figure 3. The H-bond-driven 2-D sheet extended in the crystallographic *bc* plane in **1**.

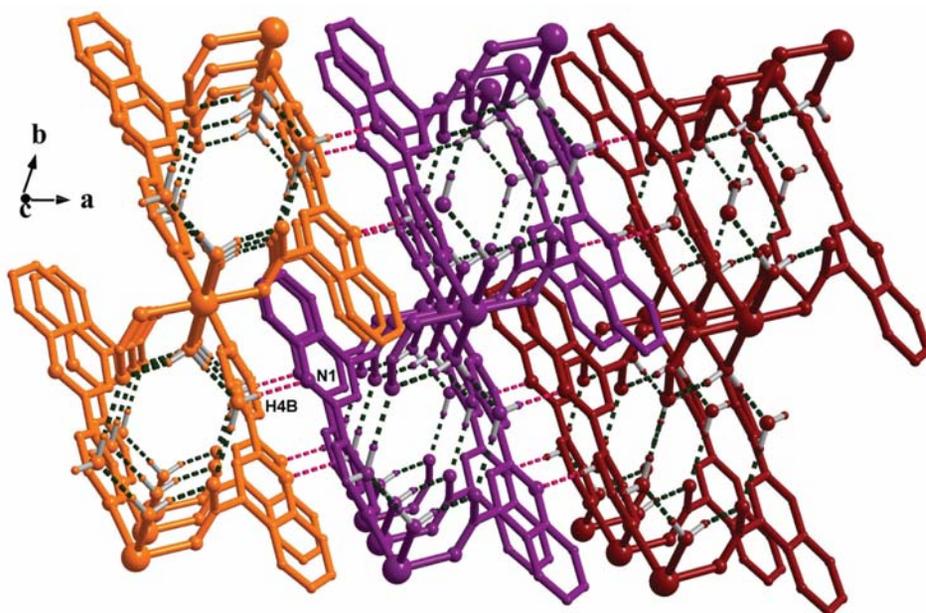


Figure 4. The 3D hydrogen-bonded network of **1**.

hydrogen bonding interactions between the coordinated water molecules and the uncoordinated carboxylic O atoms are also observed (O3–H3B...O2). Such 1D chains are aligned side by side in the *bc* plane, and the adjacent chains are held together through interchain hydrogen bonds between the coordinated water molecules and the latticed water molecules (O3–H3A...O4) into a supramolecular layer (Figure 3).

These supramolecular layers are stacked along the crystallography *a* axis as a -AA- fashion. The further O4–H4A...N2 interactions involving the latticed water molecules and the uncoordinated quinoline N atoms link these sheets into a three dimensional network (Figure 4).

Contrary to the formation of 1D infinite single-chains in complexes **1–3**, a 3D polymeric architecture of complex **4** was built when AgNO<sub>3</sub> is used for the self-as-

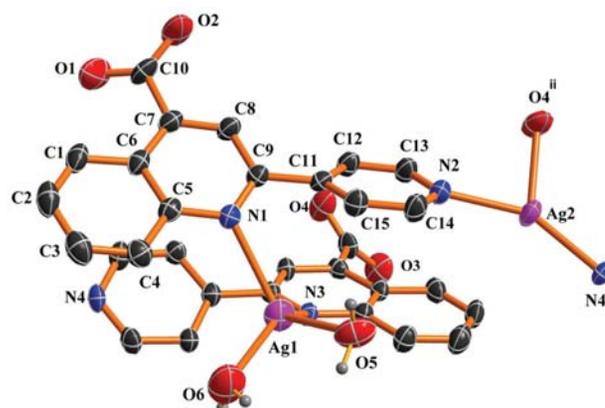


Figure 5. The coordination environment of Ag(I) in **4** at 50% probability displacement. Symmetry codes: (i)  $x + 1/2, -y + 3/2, z - 1/2$ ; (ii)  $x, -y + 1, z - 1/2$ .

Table 3 Selected Bond Distance (Å) and Angles (deg) for **4**.

|                                       |            |                         |            |
|---------------------------------------|------------|-------------------------|------------|
| Ag1–N3                                | 2.357(3)   | Ag1–O6                  | 2.437(5)   |
| Ag1–O5                                | 2.440(4)   | Ag1–N1                  | 2.494(3)   |
| Ag2–N4 <sup>i</sup>                   | 2.177(3)   | Ag2–N2                  | 2.215(4)   |
| Ag2–O4 <sup>ii</sup>                  | 2.354(3)   | O1–C10                  | 1.221(6)   |
| O2–C10                                | 1.236(6)   | O3–C25                  | 1.250(5)   |
| O4–C25                                | 1.246(6)   |                         |            |
| N3–Ag1–O6                             | 136.74(17) | N4 <sup>i</sup> –Ag2–N2 | 148.03(15) |
| N3–Ag1–O5                             | 119.33(13) | O6–Ag1–O5               | 77.77(16)  |
| N3–Ag1–N1                             | 98.09(11)  | O6–Ag1–N1               | 109.50(15) |
| O5–Ag1–N1                             | 115.95(12) | N2–Ag2–O4 <sup>ii</sup> | 88.81(13)  |
| N4 <sup>i</sup> –Ag2–O4 <sup>ii</sup> | 122.98(13) |                         |            |

Symmetry codes: (i)  $x + 1/2, -y + 3/2, z - 1/2$ ; (ii)  $x, -y + 1, z - 1/2$ .

semble reaction. Crystal structure analysis data reveal that **4** crystallizes in monoclinic system, space group *Cc*.

Two crystallographically independent Ag<sup>+</sup> ions, two deprotonated ligands L<sup>1-</sup>, two coordinated water molecules and three solvent water molecules compose the asymmetric unit of **4**. As illustrated in Figure 5, the Ag1 and Ag2 coordination environments are distinct from each other. Ag1 is four-coordinated by two water molecules (O5 and O6), and two N atoms (N3 and N1) from two quinoline rings, forming a distorted tetrahedral geometry. However, Ag2 is three-coordinated with triangle coordination geometry surrounded by two pyridine N atoms (N2 and N4<sup>i</sup>), and one monodentate carboxyl oxygen atom (O4<sup>ii</sup>). The Ag–O bond lengths are in the range of 2.354(3)–2.441(4) Å, which all fall in the normal range

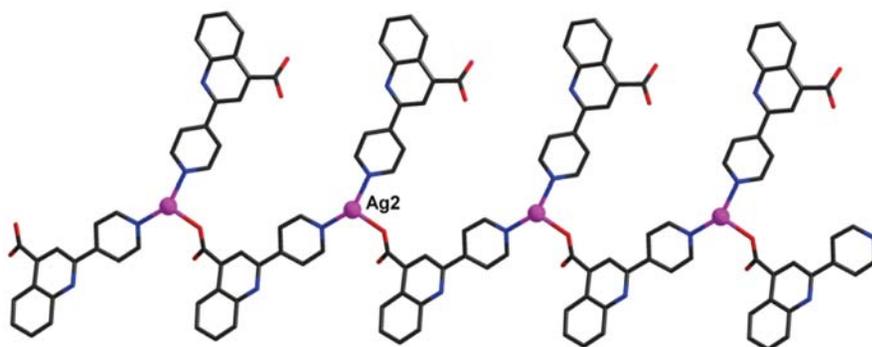


Figure 6. The one-dimensional chain structure in complex 4.

and are in agreement with those values in the previous report.<sup>21</sup>

The deprotonated ligand  $L^{1-}$  acts as bridging bidentate ligand in complexes 1–3 using the pyridine N and carboxylate O atoms. While  $L^{1-}$  displays two different coordination modes in complex 4. One kind of  $L^{1-}$  anion presents terminal bidentate coordination mode using the pyridine N2 and quinoline N1 atoms, keeping the carboxyl group uncoordinated. The coordination mode of the other kind of  $L^{1-}$  can be described as tridentate bridge, the pyridine N4, quinoline N3 and carboxyl O4 atoms are all involved in coordination.

In the structure of 4, the Ag2 cations are connected with three  $L^{1-}$  ligands to form 1D chain architecture, and the shortest Ag  $\cdots$  Ag distance is 11.318(2) Å (Figure 6). These one-dimensional chains are aligned in an -AB- fas-

hion in the crystallographic *ac* plane, and are further connected together *via* Ag1–N1 and Ag1–N3 linkages to form the 3D microporous network with circular channels along *c* axis, in which the lattice  $H_2O$  molecules are present (Figure 7).

### 3. 3. Photoluminescence Properties of HL, 3 and 4

Photoluminescence properties of the  $d^{10}$  metal complexes 3 and 4 as well as the ligand HL in dimethylsulfoxide solution were measured. Their emission spectrum is shown in Figure 8.

Upon excitation at 345 nm at room temperature, the ligand emits strong fluorescence centered at 402 nm, resulting from the ligand-centered (LC)  $\pi^*-\pi$  and  $\pi^*-n$

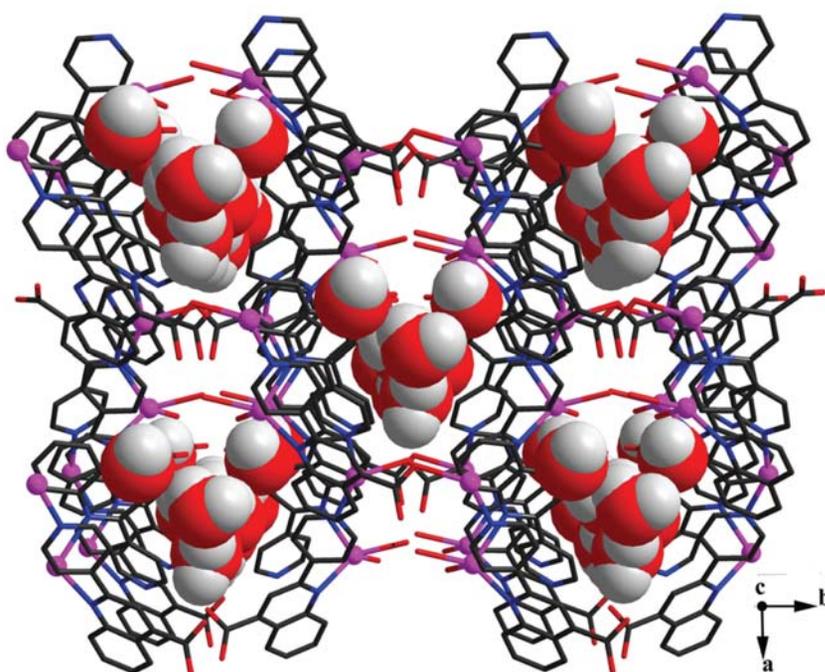


Figure 7. The 3D network of complex 4, with the water solvat molecules shown in space-filling format.

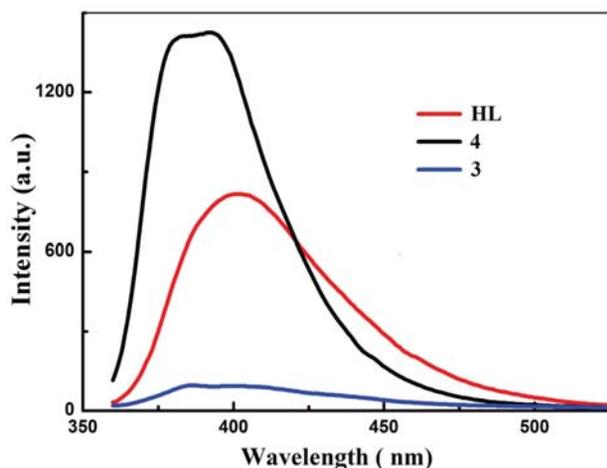


Figure 8. Photoluminescence spectra of **HL**, **3** and **4** in DMSO solution at room temperature. ( $\lambda_{\text{ex}} = 345 \text{ nm}$ )

relaxations.<sup>15</sup> Compared with **HL**, in complex **3**, a blue shift of 16 nm in the emission maxima and much weaker fluorescence intensity is observed. This is probably caused by the reduced  $\pi$ - $\pi$  conjugated effect upon coordination to the Cd(II) and the non-coplanar arrangement in **3**. The emission of complex **4** is blue shifted to 392 nm and the emission intensity is stronger than the ligand which may be ascribed to the increased rigidity of the framework.<sup>15,22</sup>

### 3. 4. Antibacterial Activities

In the present study, the *in vitro* antimicrobial properties of **HL** and its complexes **1–4** expressed as  $\text{IC}_{50}$  are presented in Table 4. Known antibiotic like streptomycin was used as control drug.

As shown in Table 4, against the all tested bacteria, free ligand **HL** and complex **1** were inactive under the tested conditions. For **2–4**, the introduction of metal ions on ligand is endowed with improved inhibition activity. Complex **2** shows its moderate activity towards gram-positive strain. Complex **3** exhibited an enhancement of antibacterial level against gram-positive strains among all the test compounds. The action of the test compounds **2**

and **3** on gram-positive bacteria is better than that on gram-negative bacteria, which is the same as Co or Cd complexes based on **HL**<sub>1</sub> and **HL**<sub>2</sub>.<sup>14,15</sup> While the antibacterial activities observed for **1–3** are all poorer than the corresponding previously reported metal complexes derived from **HL**<sub>1</sub> and **HL**<sub>2</sub>,<sup>14,15</sup> which can be ascribed to the lack of chelate effect of the carboxylic ligand in **1–3**. Ag(I) involved complex **4** exhibits activity towards gram-negative strain *P. aeruginosa* with  $\text{IC}_{50}$  value of 6.74  $\mu\text{g/mL}$ . This selective activity can be attributed to the nature of the Ag ion.<sup>21,23</sup>

## 4. Conclusions

Chain like Mn(II), Co(II) and Cd(II) complexes and 3D network Ag(I) complex with the quinoline carboxylic ligand 2-(pyridin-4-yl)quinoline-4-carboxylic acid were synthesized and their crystal structures were determined. The ligand and its Cd(II) and Ag(I) complexes are luminescent with maximum emission wavelength at 402 nm, 386 nm and 382 nm, respectively. The compounds were screened for their antibacterial activity. The bioassay results indicate that Co(II) and Cd(II) complexes exhibit antibacterial activity against gram-positive bacteria *B. subtilis* and *S. aureus*, and Ag(I) complex exhibits antibacterial activity against *P. aeruginosa*. The present observations demonstrate that the modulation of antibacterial activity can be achieved by the coordination geometrical shape and the nature of the central atoms.

## 5. Supplementary Material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Center as supplementary publication Nos. CCDC 1456423 (**1**), 1456422 (**2**), 1456421 (**3**) and 1496618 (**4**). Copies of the data can be obtained free of charge via [www.ccdc.ac.uk/conts/retrieving.html](http://www.ccdc.ac.uk/conts/retrieving.html) (or from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, Fax: +44-1223-336-033. E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

Table 4. Antimicrobial activity of the tested compounds.

| Compounds    | Half maximal inhibitory concentrations ( $\mu\text{g/mL}$ ) |                     |                   |                 |
|--------------|---|---------------------|-------------------|-----------------|
|              | Gram-negative   |                     | Gram-positive     |                 |
|              | <i>E.coli</i>   | <i>P.aeruginosa</i> | <i>B.subtilis</i> | <i>S.aureus</i> |
| <b>HL</b>    | –   | –                   | –                 | –               |
| <b>1</b>     | –   | –                   | –                 | –               |
| <b>2</b>     | –   | –                   | 18.21             | 20.59           |
| <b>3</b>     | –   | –                   | 11.24             | 1.87            |
| <b>4</b>     | –   | 6.74                | –                 | –               |
| Streptomycin | 3.81  | –                   | 3.42              | 4.62            |

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## Povzetek

Štiri kovinske komplekse s kinolinkarboksilatnim ligand iz 2-(piridin-4-il)kinolin-4-karboksilne kisline (**HL**),  $\{[ML_2(H_2O)_2] \cdot 2H_2O\}_n$  ( $M = Mn^{II}$ , **1**;  $M = Co^{II}$ , **2**;  $M = Cd^{II}$ , **3**) in  $\{[Ag_2L_2(H_2O)_2] \cdot 3H_2O\}_n$  (**4**) smo sintetizirali z uporabo hidrotermalnih pogojev. Spojine smo okarakterizirali s pomočjo elementne analize, IR spektroskopije ter določili strukture z monokristalno rentgensko difrakcijo. Kompleksi **1–3** imajo 1D veržno strukturo, ki je nadalje preko vodikovih vezi medsebojno povezana, da tvori 3D supramolekularno mrežo. Kompleks **4** ima 3D strukturo. Raziskali smo tudi fluorescenčne lastnosti in antibakterijsko aktivnost teh spojin.