

Article

Synthesis, Molecular, and Supramolecular Structures of Two Azide-Bridged Cd(II) and Cu(II) Coordination Polymers

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Abstract: Two 1D coordination polymers were synthesized by reaction of two ligands, 2-amino-4-picoline (**2A4Pic**) and quinoline-6-carboxylic acid (**Qu-6-COOH**) with two metal (II) nitrate (M = Cd and Cu) in the presence of azide as a linker. The synthesized metal complexes [**Cd(2A4Pic)₂(N₃)₂**]_n; (**1**) and [**Cu(Qu-6-COO)(N₃)(H₂O)**]_n; (**2**) were isolated in single crystals and their X-ray structures revealed a 1D polymeric structure. Due to symmetry considerations, the asymmetric formula is half a [**Cd(2A4Pic)₂(N₃)₂**] unit for **1** and one [**Cu(Qu-6-COO)(N₃)(H₂O)**] unit for **2**. In complex **1**, the Cd(II) is hexa-coordinated with two **2A4Pic** molecules and four $\mu(1,1)$ azide units. Hence, the CdN₆ coordination environment has a slightly distorted octahedral geometry. In **2**, the Cu(II) is hexa-coordinated with three different ligands (**Qu-6-COO[−]**, **H₂O** and $\mu(1,1)$ **N₃[−]**) where all are connectors between the crystallographically related Cu(II) sites. Additionally, complex **2** distorted CuN₂O₄ octahedral geometry. In both complexes, the polymer arrays are connected by N ... H hydrogen bonds and π - π stacking interactions. Based on Hirshfeld analysis, the percentages of N ... H contacts are 43.1 and 27.4% for **1** and **2**, respectively, while %C...C are 5.6 and 9.3%, respectively. Analysis of Cu-N, Cu-O, and Cd-N bonds using DFT calculations showed predominantly closed-shell coordination interactions with little covalent characters. Additionally, the negatively charged ligand groups were found to compensate the positive charge of the central metal ion to a larger extent than the electrically neutral ligands.

Keywords: coordination polymer; azide; pyridine; quinoline; Hirshfeld



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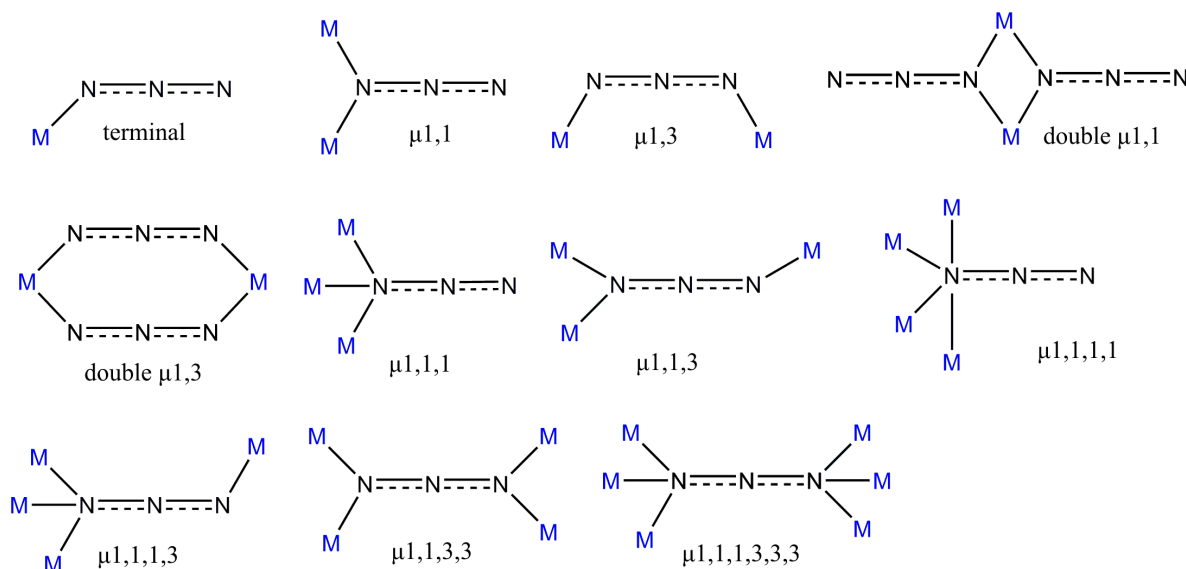
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1. Introduction

Coordination polymers (CPs) attracted too much attention from researchers due to their wide range of applications [1–6]. These compounds were applied in a variety of fields, including gas adsorption [7,8], catalysis [9,10], and drug delivery [9,11]. Additionally, many CPs are interesting magnetic materials [12] and were used in device fabrication [13,14] and molecular sensing [7,15–18]. Other notable applications of CPs are their uses in solar cells, Schottky barrier diodes (SBD), and other electronic and opto-electronic devices [13,19–22].

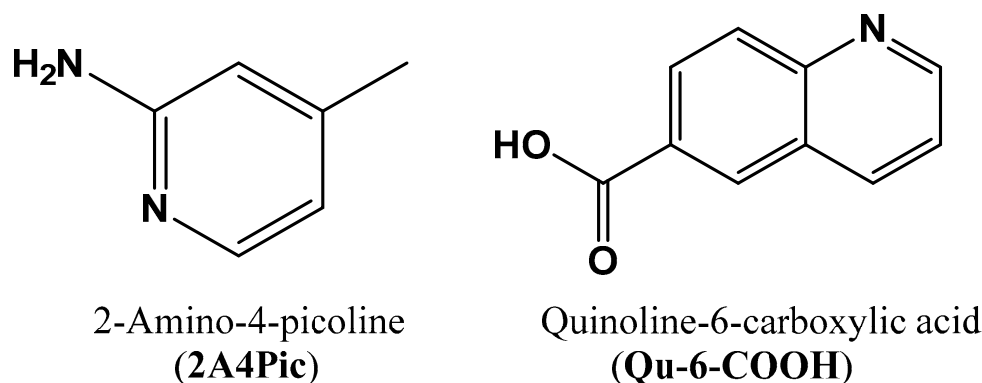
On the other hand, structural flexibility and electronic characteristics of the organic ligand, and also nature of metal ion are important factors for construction of CPs [23,24]. In addition, the dimensionality of CPs could be enhanced by selection of suitable linkers. Azide and carboxylate anions are interesting bridging ligands because of their structural versatility in coordination chemistry [25–31]. Azide ion is a highly symmetric anion that has small size and linear shape. Hence, it has a high ability to propagate the magnetic

interactions between paramagnetic centers, leading to CPs with interesting magnetic properties [6,32,33]. Additionally, the coordinated azide has two N-N bonds, which are less symmetric compared to the free one where the degree of asymmetry depends on the azide bonding mode. Among the pool of bonding modes of azide ion (Scheme 1), the end-on ($\mu(1,1)$ or EO) and end-to-end ($\mu(1,3)$ or EE) are the most prevalent [6,32,33]. These bridging modes are responsible for the construction of coordination compounds with varying nuclearity and dimensionality [32–38]. In this regard, many fascinating and structurally attractive Cu(II) [39–41] and Cd(II) [42–50] complexes were constructed. Additionally, carboxylate ligands are extremely versatile linkers because of their different coordination modes [31].



Scheme 1. Different bonding modes of the azide ion.

In the light of the exciting coordination chemistry of azide ion as a linker [51], the current work aims to synthesize new azido CPs comprising 2-amino-4-picoline (**2A4Pic**) and quinoline-6-carboxylic acid (**Qu-6-COOH**) (Scheme 2). Their molecular and supramolecular structure features were described. Theoretical studies were performed to describe the nature and strength of the metal–ligand interactions.



Scheme 2. Structure of the ligands used.

2. Materials and Methods

All chemicals, physicochemical characterizations, and details of solving the X-ray structure [52,53] are described in Supplementary data.

2.1. Synthesis of $[\text{Cd}(\text{2A4Pic})_2(\text{N}_3)_2]_n$ (1)

2-Amino-4-picoline (21.6 mg, 0.2 mmol) in 10 mL EtOH was added to $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (30.8 mg, 0.1 mmol) solution in 10 mL distilled water followed by adding 0.5 mL saturated NaN_3 aqueous solution drop wisely, then the clear mixture was left for slow evaporation at ambient conditions. After five days, complex **1** was formed as colorless needle crystals.

$[\text{Cd}(\text{2A4Pic})_2(\text{N}_3)_2]_n$; (**1**) (69% yield). Anal. Calc. $\text{C}_{12}\text{H}_{16}\text{CdN}_{10}$: C, 34.92; H, 3.91; N, 33.94; and Cd, 27.24%. Found: C, 34.74; H, 3.83; N, 33.61; and Cd, 27.07%.

2.2. Synthesis of $[\text{Cu}(\text{Qu-6-COO})(\text{N}_3)(\text{H}_2\text{O})]_n$ (2)

Quinoline-6-carboxylic acid (17.4 mg, 0.1 mmol) in 10 mL EtOH was added to $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (24.2 mg, 0.1 mmol) in 10 mL EtOH followed by dropwise addition of 0.5 mL of saturated NaN_3 aqueous solution, then the slightly turbid solution was filtered and the clear filtrate was allowed to slowly evaporate at ambient conditions. Complex **2** was obtained as dark green plate crystals after one week.

$[\text{Cu}(\text{Qu-6-COO})(\text{N}_3)(\text{H}_2\text{O})]_n$; (**2**) (66% yield) Anal. Calc. $\text{C}_{10}\text{H}_8\text{CuN}_4\text{O}_3$: C, 40.61; H, 2.73; N, 18.94; and Cu, 21.49%. Found: C, 40.49; H, 2.66; N, 18.72; and Cu, 21.35%.

2.3. Hirshfeld and DFT Calculations

Details regarding Hirshfeld [54] and DFT computations are described in Supplementary data [55–61].

3. Results and Discussion

3.1. X-ray Crystal Structure Description of **1**

Structure of the asymmetric unit and the coordination environment of $[\text{Cd}(\text{2A4Pic})_2(\text{N}_3)_2]_n$ (**1**) is shown in Figures 1A and 2A, respectively. The crystal system of **1** is monoclinic and the space group is $P2_1/c$. The unit cell parameters are $a = 8.9157(3)$ Å, $b = 3.69130(10)$ Å, $c = 23.1784(7)$ Å, and $\beta = 90.0980(10)^\circ$, while $Z = 2$ and $V = 762.81(4)$ Å³ (Table 1). The structure of this highly symmetric complex comprised only a half $[\text{Cd}(\text{2A4Pic})_2(\text{N}_3)_2]$ unit per asymmetric formula (Figure 1).

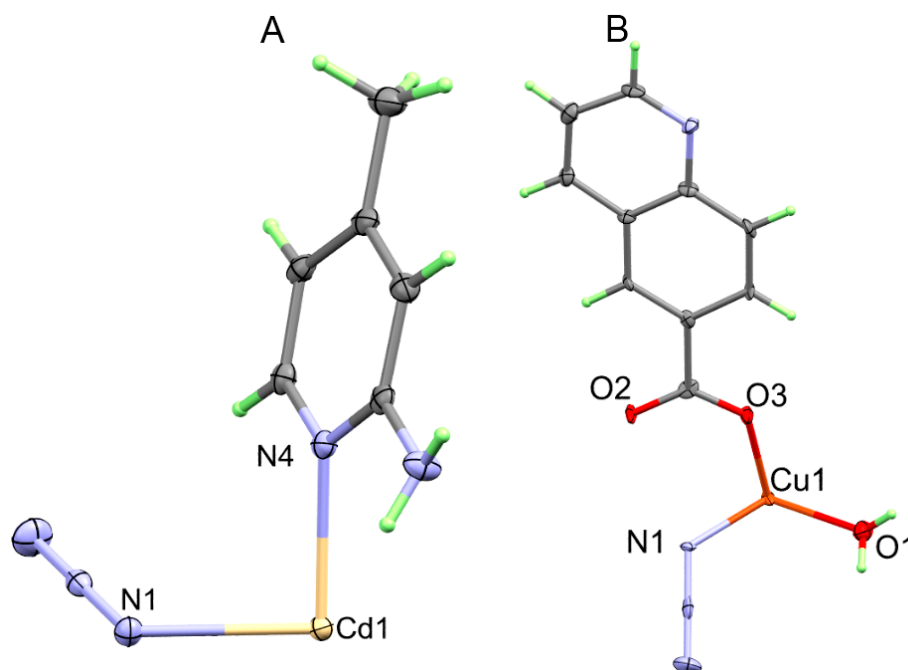


Figure 1. Structure of asymmetric unit of complexes **1** (A) and **2** (B).

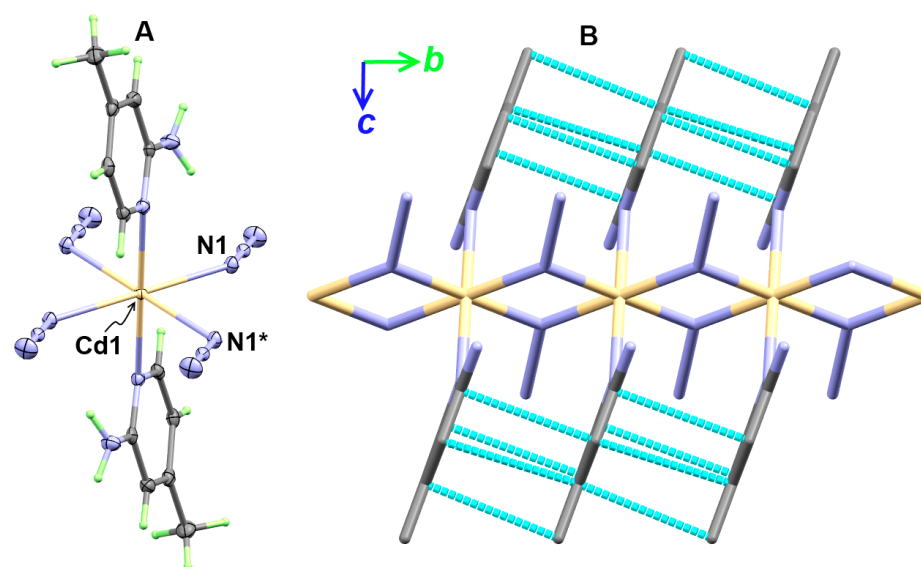


Figure 2. The coordination environment (A) and structure of the 1D polymer (B) of **1**. Symmetry code for N1* is 2-x,2-y,-z. All H-atoms were omitted from the right part of this illustration for better clarity.

Table 1. Crystallographic details for **1** and **2**.

Complex	1	2
Empirical formula	C ₁₂ H ₁₆ Cd N ₁₀	C ₁₀ H ₈ Cu N ₄ O ₃
F.Wt	412.75 g/mol	295.74 g/mol
T	100(2) K	100(2) K
λ	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions (Å, °)	<i>a</i> = 8.9157(3) <i>b</i> = 3.69130(10) <i>c</i> = 23.1784(7) β = 90.0980(10)	<i>a</i> = 8.0773(5) <i>b</i> = 6.4187(3) <i>c</i> = 20.9267(12) β = 96.499(2)
<i>V</i> (Å ³)	762.81(4)	1077.99(10)
<i>Z</i>	2	4
ρ_{calc} (g/cm ³)	1.797	1.822
μ (Mo K α) (mm ^{−1})	1.448	2.032
Θ -range (°)	2.88 to 26.43	2.54 to 23.35
No. Reflns	7030	10351
Indep. reflns	1543 [<i>R</i> _(int) = 0.0248]	1542 [<i>R</i> _(int) = 0.0775]
%Completeness to Θ	97.80	98.80
GOOF (<i>F</i> ²)	1.098	1.050
Final <i>R</i> [<i>I</i> > 2sigma(<i>I</i>)]	<i>R</i> ₁ = 0.0166, <i>wR</i> ₂ = 0.0387	<i>R</i> ₁ = 0.0367, <i>wR</i> ₂ = 0.0770
<i>R</i> (all data)	<i>R</i> ₁ = 0.0190, <i>wR</i> ₂ = 0.0398	<i>R</i> ₁ = 0.0721, <i>wR</i> ₂ = 0.0925
CCDC	2207079	2207080

The Cd(II) ion is coordinated with two **2A4Pic** ligand units and four N₃[−] groups where each two *trans* Cd–N bonds are equidistant due to symmetry consideration. The Cd to N distance with **2A4Pic** is 2.3305(15) Å. The azide group has a $\mu(1, 1)$ bonding mode and it acts as a linker between the Cd(II) centers via Cd1–N1 and Cd1–N1* bonds. The corresponding Cd–N distances are 2.3496(15) and 2.4198(15) Å, respectively. Similar to **1**, the structurally related [Cd(3-acetylpyridine)₂(N₃)₂]_n 1D polymer has only $\mu(1,1)$ bridging azide, while the [Cd(4-ethylpyridine)₂(N₃)₂]_n, [Cd(4-hydroxymethylpyridine)₂(N₃)₂]_n, [Cd(3-hydroxymethylpyridine)₂(N₃)₂]_n [62], and [Cd(4-azidopyridine)₂(N₃)₂]_n complexes [63] are 1D polymer but with mixed $\mu(1,1)$ and $\mu(1,3)$ bridged azides. Hence, nature of the substituent at the pyridine ring has a significant impact on the azide bonding mode. In

[Cd(4-azidopyridine)₂(N₃)₂]_n complex, the Cd-N distances with the $\mu(1,1)$ bridged azide are found to be 2.3371(17) and 2.3442(18) Å, which are very close to the corresponding Cd-N distances in **1** [63]. Hence, the structure of **1** is a 1D coordination polymer extended along the crystallographic *b*-direction (Figure 2). As can be seen from this figure, the coordinated azide groups form with Cd(II) the four membered (Cd1N1)₂ ring, in which the N1-Cd1-N1 and Cd1-N1-Cd1 angles are 78.59(5)° and 101.41(5)°, respectively. The organic ligand units were found almost perpendicular to the extension of the coordination polymer and distributed above and below the 1D polymer array where the angle between the pyridine and the (Cd1N1)₂ rings is 72.68°. All the *trans* N-Cd-N angles are perfectly the same as for ideal octahedron (180°) while the *cis* N-Cd-N angles are slightly deviated from the ideal value of 90° (Table 2).

Table 2. The important distances (Å) and angles (°) for complex **1**.

Bond	Distance	Bond	Distance
Cd1-N4	2.3305(15)	Cd1-N1 ¹	2.4198(15)
Cd1-N1	2.3496(15)		
Bonds	Angle	Bonds	Angle
N1-Cd1-N1 ²	180.00(8)	N4-Cd1-N1 ¹	92.79(5)
N4 ¹ -Cd1-N4	180	N4-Cd1-N1 ³	87.21(5)
N4-Cd1-N1	91.80(5)	N1-Cd1-N1 ¹	78.59(5)
N4-Cd1-N1 ²	88.20(5)	N1-Cd1-N1 ⁴	101.41(5)

¹ 2-X,3-Y, -Z; ² 2-X,2-Y, -Z; ³ +X, -1+Y,+Z; and ⁴ +X,1+Y,+Z.

As clearly seen in Figure 2, different levels of π - π stacking between the pyridine groups were detected. The shortest contact distances are C2 ... C1 (3.506 Å), C3 ... C2 (3.544 Å), C3 ... C6 (3.510 Å), and C4 ... C5 (3.509 Å), while the corresponding centroid-centroid distance is 3.691 Å. In addition, the coordination polymer arrays are interconnected with each other along the crystallographic *a*-direction via N5-H1A ... N3 bridges between the amino group as the H-bond donor and the freely uncoordinated N-atom from the N₃[−] group (Figure 3). The H1A ... N3 and N5 ... N3 distances are 2.37(3) and 3.184(2) Å, respectively, while the N5-H1A ... N3 angle is 167(2)°.

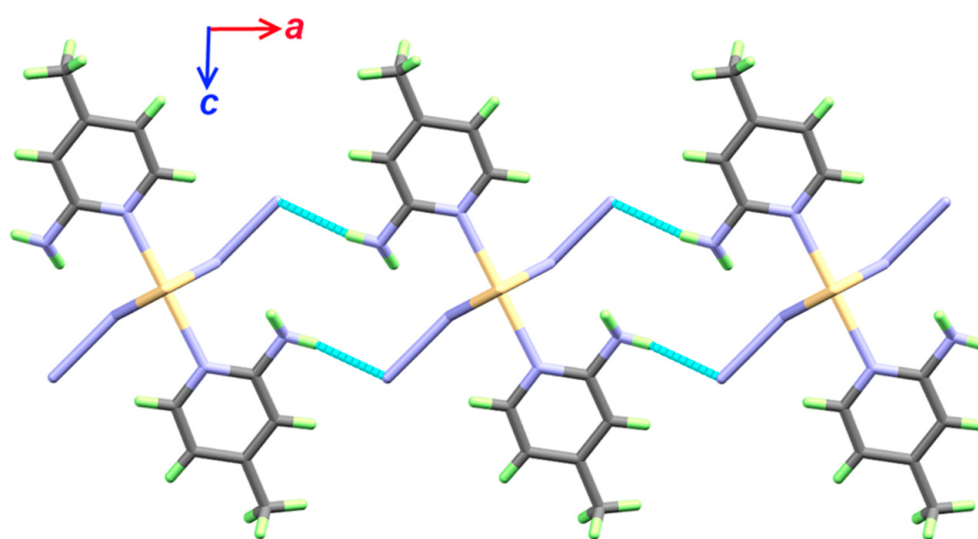


Figure 3. The hydrogen bond polymer in [Cd(2A4Pic)₂(N₃)₂]_n complex.

3.2. X-ray Crystal Structure Description of **2**

The X-ray structure analysis showed a polymeric structure for the [Cu(Qu-6-COO)(N₃)(H₂O)]_n complex (**2**). The asymmetric formula represents one [Cu(Qu-6-COO)(N₃)(H₂O)] unit as

shown in Figure 1B. The crystal system of **2** is monoclinic and space group is $P2_1/c$. The unit cell parameters are $a = 8.0773(5)$ Å, $b = 6.4187(3)$ Å, $c = 20.9267(12)$ Å, and $\beta = 96.499(2)^\circ$, while $Z = 4$ and $V = 1077.99(10)$ Å³ (Table 1). The Cu(II) is hexa-coordinated, but in this case, there are three types of ligands that are the quinoline-6-carboxylate anion, azide group, and the water molecule, where all are acting as bridging ligands connecting the crystallographically related Cu(II) sites along the b -direction. Each Cu(II) is coordinated with two sets of these ligands, and due to symmetry consideration, each two similar ligand units are anti to one another (Figure 4A). The quinoline-6-carboxylate ligand is found coordinated by two Cu(1) ions via the carboxylate oxygen atoms O2 and O3 in the *syn-syn* geometry [64]. The corresponding Cu-O distances are 1.945(3) and 1.946(4) Å, respectively. In the structurally related [Cu(2-Chloro-6-methylnicotinate)(N₃)(MeOH)]_n complex, the bridged carboxylate forms two Cu-O bonds with very close distances as in complex **2**. In this case, the Cu-O distances were found to be 1.953(1) to 2.010(1) Å [64]. Additionally, the water molecule is bridging the Cu(1) sites via the two significantly different Cu1-O1 (2.374(4) Å) and Cu1²-O1 (2.771(3) Å) bonds (Table 3). Bridging water ligands in such complexes are not common. A bridging H₂O ligand was found in the [Ni₂(H₂O)(4-amino-3,5-dimethyl-1,2,4-triazole)₂(pivalate)₄(H₂O)₂] complex [65]. It is worth noting that the bridged water metal complexes are not common in literature. For example, the bridged H₂O was found in [Ni₂(H₂O)(4-amino-3,5-dimethyl-1,2,4-triazole)₂(pivalate)₄(H₂O)₂] complex [65]. Additionally, the penta-nuclear [Ag₅(PTDM)₄(H₂O)₆(ClO₄)₄]ClO₄ complex, where PTDM is 4,4'-[6-(3,5-dimethyl-1H-pyrazol-1-yl)-1,3,5-triazine-2,4-diyl]dimorpholine, comprised a bridged water structure [66]. The coordination environment of Cu(1) in **2** is completed by interaction with two azide groups, which have a $\mu(1,1)$ mode. The two Cu-N bond distances that occurred between the bridged azide and Cu(II) are marginally different (Cu1-N1: 1.986(4) and Cu1-N1¹: 1.995(4) Å) [64]. Hence, the structure of **2** is a 1D coordination polymer extended along the b -direction (Figure 4B). The donor atoms N1 and O1 form with Cu1 the four membered ring N1Cu1O1Cu1, in which the O1-Cu1-N1 angles range from 78.1(1) to 88.5(1)° while the Cu-N-Cu and Cu-O-Cu angles are 108.7(2) and 77.6(1)°, respectively. The *trans* N1-Cu1-N1, O1-Cu1-O1, and O2-Cu1-O3 angles are 166.1(2), 175.7(1), and 178.2(1)°, respectively. Hence, the CuN₂O₄ coordination geometry is distorted octahedron.

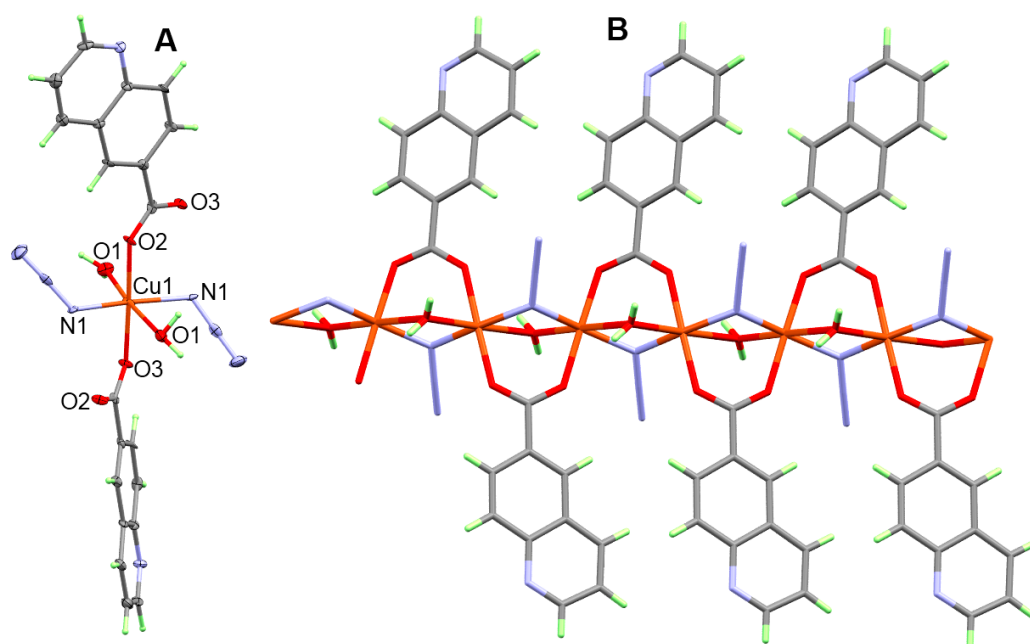


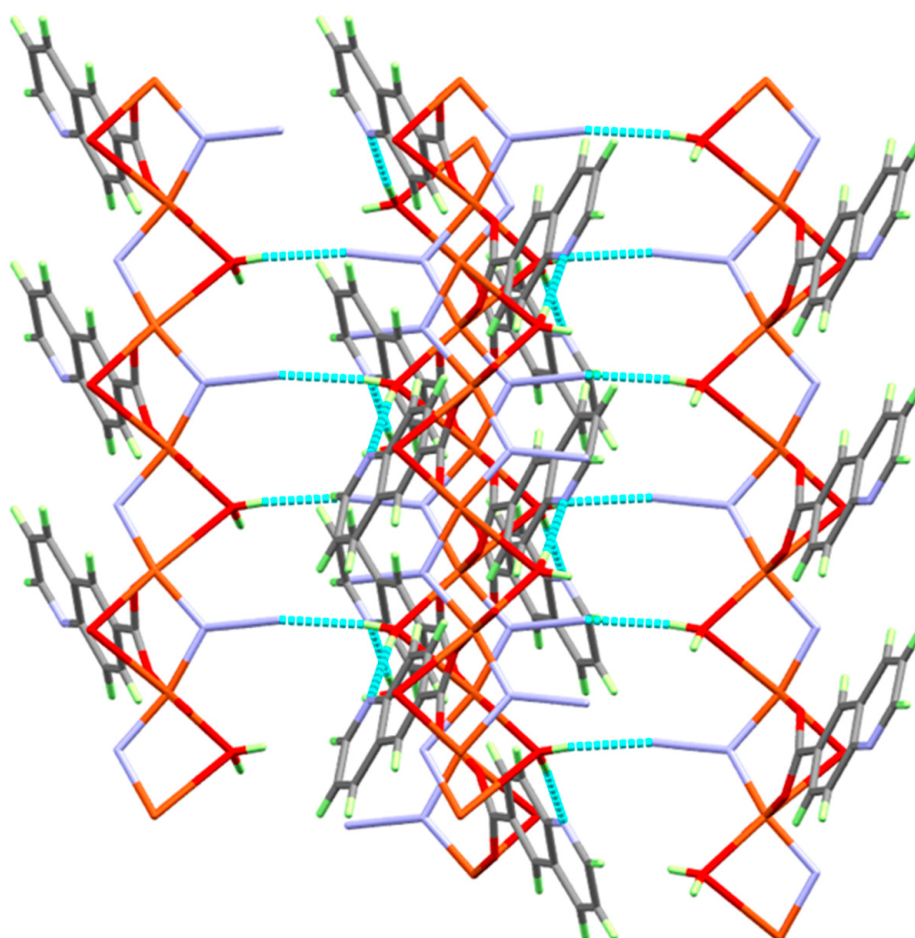
Figure 4. The coordination environment (A) and structure of the 1D polymer (B) of **2**. All H-atoms were omitted from the right part of this illustration for better clarity.

Table 3. The important distances (Å) and angles (°) for complex **2**.

Bond	Distance	Bond	Distance
Cu1-O2	1.945(3)	Cu1-N1 ¹	1.995(4)
Cu1-O3	1.946(3)	Cu1-O1	2.374(4)
Cu1-N1	1.988(4)	Cu1 ² -O1	2.771(3)
Bonds	Angle	Bonds	Angle
O2-Cu1-O3	178.22(14)	N1-Cu1-N1 ¹	166.14(12)
O2-Cu1-N1	86.97(15)	O2-Cu1-O1	83.93(13)
O3-Cu1-N1	91.46(15)	O3-Cu1-O1	95.69(13)
O2-Cu1-N1 ¹	91.34(15)	N1-Cu1-O1	105.02(15)
O3-Cu1-N1 ¹	90.39(15)	N1 ¹ -Cu1-O1	88.46(15)

¹ 2−X, 1/2+Y, 1/2−Z; ² 2−X, −1/2+Y, 1/2−Z.

The N4 atom of Qu-6-COO[−] and the free N3 atom of N₃[−] ion do not participate in the coordination with Cu(II) ion. These N-sites are acting as H-bond acceptors, which form strong O1-H1...N3 and O1-H2...N4 H-bridges with the coordinated H₂O molecule as the H-bond donor. The H1...N3 and H2...N4 distances are 2.26(3) and 1.98(4) Å, respectively, while the O1 ... N3 and O1 ... N4 donor–acceptor distances are 3.079(6) and 2.799(5) Å, respectively. The respective donor–H–acceptor angles are 163(5) and 169(4)°, respectively. The hydrogen bond network is presented in Figure 5.

**Figure 5.** The hydrogen bond polymer in [Cu(Qu-6-COO)(N₃)(H₂O)]_n complex.

In addition, there are a number of π – π stacking interactions which connect the 1D chains via short C5 ... C8 (3.396 Å), C3 ... C10 (3.327 Å), and C6 ... C8 (3.320 Å) interac-

tions, while the centroid–centroid distance is 3.687 Å. These results confirm the presence of significant π – π stacking interactions between the quinoline rings (Figure 6).

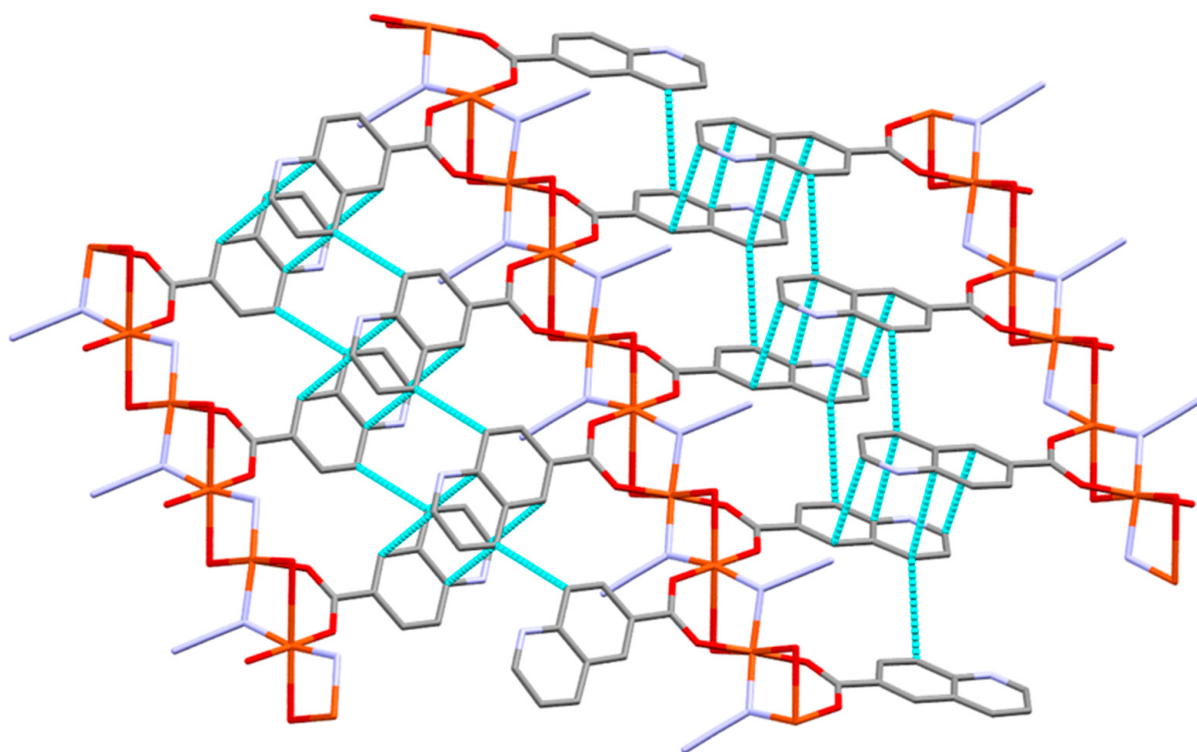


Figure 6. The π – π stacking interactions in $[\text{Cu}(\text{Qu-6-COO})(\text{N}_3)(\text{H}_2\text{O})]_n$ complex.

3.3. Hirshfeld Analysis of Molecular Packing

X-ray structures of **1** and **2** revealed 1D coordination polymeric structures for both complexes. Hence, Hirshfeld calculations were performed on the $[\text{Cd}(\text{2A4Pic})_2(\text{N}_3)_4]$ and $[\text{Cu}(\text{Qu-6-COO})(\text{N}_3)(\text{H}_2\text{O})]$ complex units. Decomposition analysis of the different intermolecular contacts is shown in Figure 7, while their percentages are listed in Table S1 (Supplementary Materials). It is shown that the largest contributions are related to the N...H (43.1, 27.4%) and H...H (34.5, 27.1%) interactions for complexes **1** and **2**, respectively.

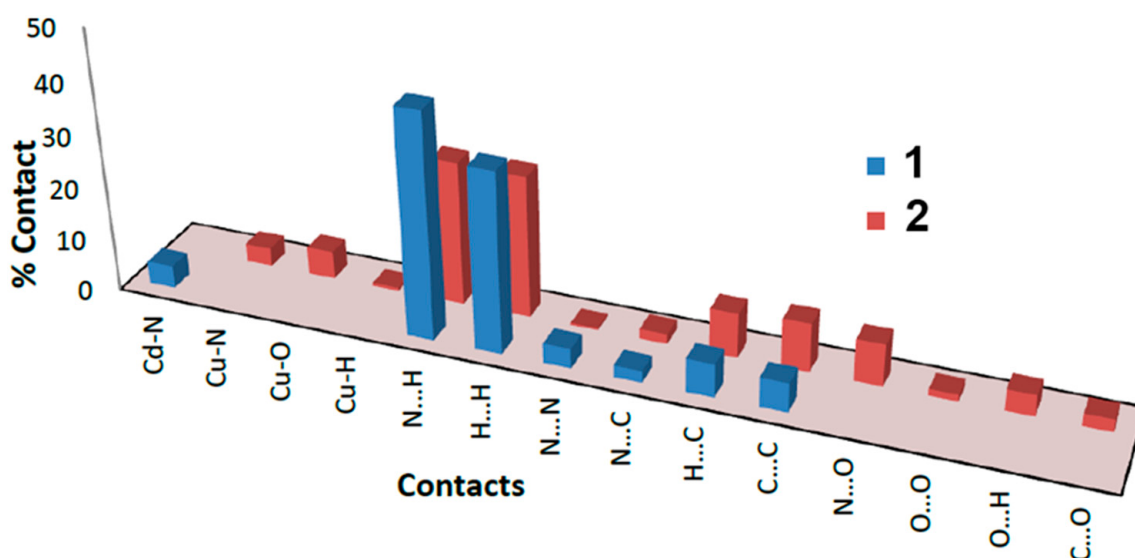


Figure 7. All intermolecular contacts in compounds **1** and **2**.

For complex **1**, many N ... H and H...H contacts are contributed in the molecular packing and crystal stability. Their d_{norm} surfaces and fingerprint (FP) plots showed large intense red spots and sharp spikes, respectively (Figure S1, Supplementary Materials). The H...H contacts appeared as red spots, where all are related to H7 ... H8 interaction with interaction distance of 2.101 Å. On the other hand, the N1 ... H2 interaction is the shortest N ... H contact (2.164 Å). Other longer contacts, such as N3 ... H1 (2.203 Å) and N2 ... H5 (2.565 Å) were also observed as red spots in the d_{norm} surface. It is worth mentioning that the shape index and curvedness maps can give good indications on the presence of aromatic π - π stacking interactions. The red/blue triangles in the former and the flat green area in the latter are clearly evident from Figure S2, (Supplementary Materials). These criteria are achieved in complex **1**, which revealed the π - π stacking between the organic ligand units. Additionally, the Cd-N coordination interactions represent 4.3% from the total fingerprint area of complex **1**. It is clear from the d_{norm} surface that the Cd-N interactions appeared as intense red spots, which confirm the polymeric structure of this complex via the azide ion as a linker (Figure 8).

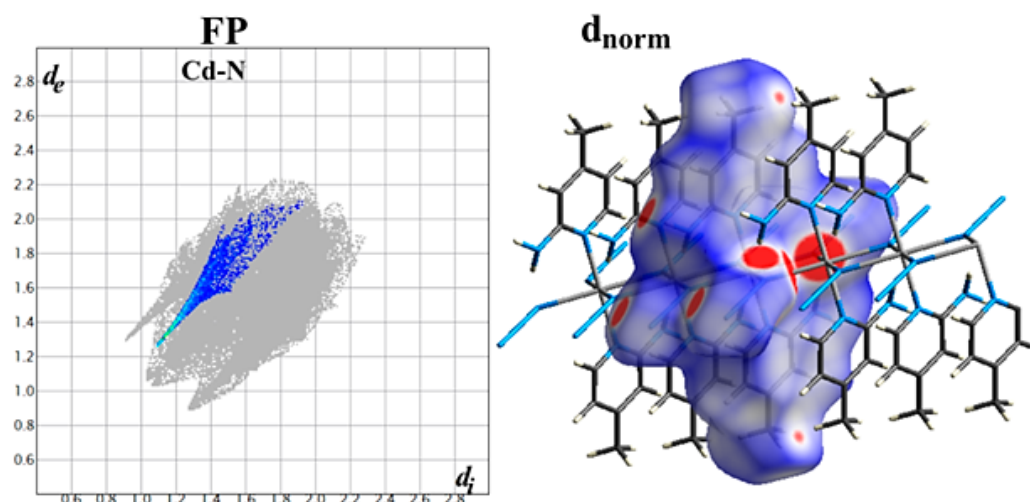


Figure 8. The overall d_{norm} map (right) and decomposed fingerprint plot (left) for the Cd-N coordination interactions in complex **1**.

For complex **2**, the decomposition of the different contacts also revealed the polymeric nature of this complex via Cu-N and Cu-O coordination interactions. The intense red regions in the d_{norm} map close to the central Cu(II) are related to the coordination interactions with the bridged azido, carboxylate, and water ligand groups, which form the 1D polymeric chain of this complex. The %Cu-O and %Cu-N interactions are 5.3 and 3.5%, respectively. Additionally, the Cu-O and Cu-N interactions appeared as sharp spikes in the FP plots (Figure 9). Other contacts, such as N ... H (27.4%), C...C (9.3%), and N...O (8.1%) are important for the crystal stability of complex **2** (Figure S3, Supplementary Materials). Additionally, the presence of the significant amount of C...C contacts, along with the red/blue triangles in the SI map related to the coordinated quinoline moiety confirm the presence of π - π stacking interactions (Figure S4, Supplementary Materials). The C10 ... C3 (3.329 Å) and C6 ... C8 (3.319 Å) are the shortest. Other important short interactions are listed in Table 4.

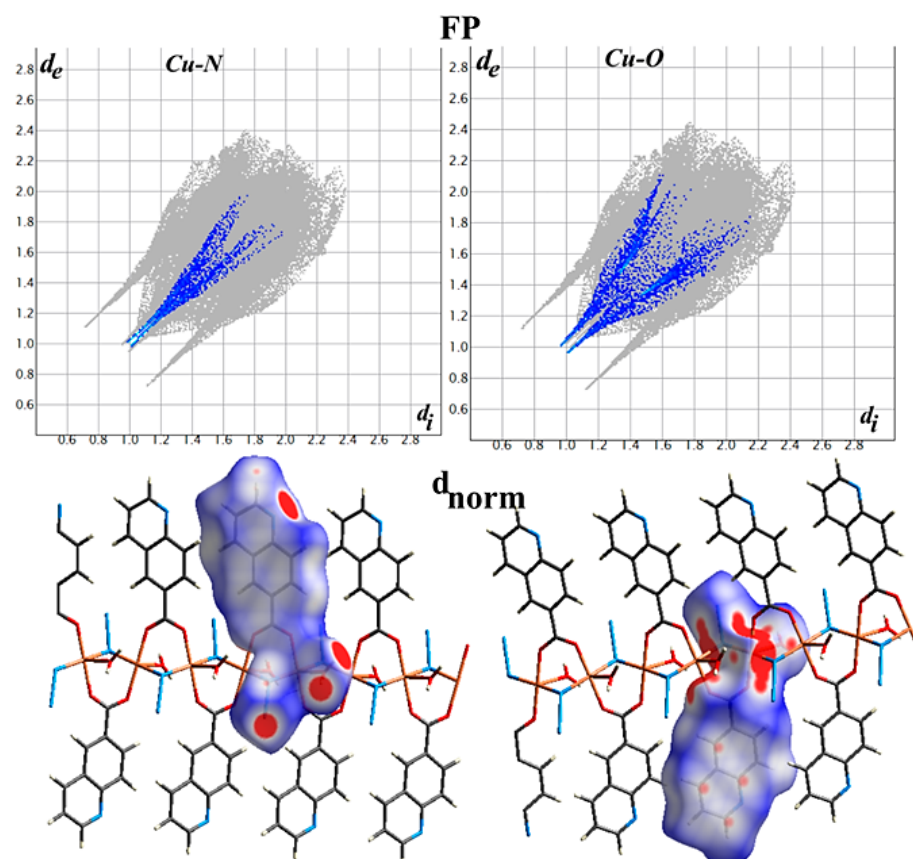


Figure 9. Hirshfeld d_{norm} surface (**lower**) and FP plot (**upper**) reveal the polymeric structure of complex **2** via Cu-N and Cu-O coordination interactions.

Table 4. The short interactions and their distances in complex **2**.

Contact	Distance	Contact	Distance
C10 ... C3	3.327(7)	N4 ... H2	1.827
C6 ... C8	3.320(7)	N2 ... H10	2.586
C5 ... C8	3.396(7)	N3 ... H1	2.121
Cu1-N1	1.995(4)	N2 ... O2	2.828(5)
Cu1-O2	1.945(3)	N2 ... O3	2.857(5)
Cu1-O1	2.771(3)		

3.4. The Atoms in Molecules (AIM) Analysis

The AIM analysis is widely used to describe the nature and strength of bonding in different types of molecules [67,68]. The AIM theory is extensively applied to differentiate between covalent and noncovalent interactions [69,70]. The properties of the coordinate bonds were described based on electron density $\rho(r)$, its laplacian $\nabla^2\rho(r)$, kinetic energy density $G(r)$, potential energy density $V(r)$, and kinetic energy of the Hamiltonian $H(r) = G(r) + V(r)$ at the bond critical points (BCPs) [71,72]. These topological parameters are listed in Table S2 (Supplementary Materials). Our results generally demonstrate the mainly closed-shell character of all coordinate bonds in both complexes because $\rho(r)$ values are less than 0.1 a.u. along with the small positive value of $\nabla^2\rho(r)$. In accordance with the observed shorter Cu-O_(carboxylate) (1.945 and 1.946 Å) bond distances than the Cu-O_(water) (2.771 and 2.374 Å) bonds in complex **2**, the $\rho(r)$ and $\nabla^2\rho(r)$ of the former are larger than those for the latter [73]. Additionally, the $H(r)$ parameter at the BCPs has small negative values, which are close to zero, indicating the presence of little covalent characters in the studied Cd-N, Cu-N, and Cu-O coordinate bonds. Additionally, the results reveal the higher covalent

characters for the Cu-O_(carboxylate) bonds than the Cu-O_(water) bonds in complex **2**, where the H(r) values for the former are significantly more negative (−0.0153 and −0.0157 a.u.) than those for the latter.

3.5. Natural Population Analysis

One of the best models for calculating the charge population is the natural charge analysis [74]. In transition metal complexes, the interaction between the ligand groups and metal ion affect the charges of these fragments. The charges of the central metal ion in the two complexes are changed significantly after complexation. The charge of the Cd(II) and Cu(II) ions are changed to 1.0374 e and 0.9199 e in complexes **1** and **2**, respectively. As a result, the amounts of electron density transferred from the ligands to metal ion are 0.9626 and 1.0801 e, respectively. In complex **1**, the calculated charges transferred from each N₃[−] and 2A4Pic units were estimated to be 0.1948 and 0.0918 e (average values), respectively. In complex **2**, the net charge of the Qu-6-COO[−], N₃[−], and H₂O ligand groups are estimated to be −0.8032, −0.7176, and 0.0608e, respectively. As a result, the water molecule transferred the lowest amount (0.0608 e) of electron density to Cu(II) cation, while the N₃[−] ligand transferred the largest amount (0.2824 e). In addition, each Qu-6-COO[−] transferred 0.1968 e to the Cu(II) ion. It is also noticed that each coordinated azide transferred a higher amount of electron density to the metal ion in complex **1** than **2**. The reason might be explained in terms of the higher compensation of the positive charge of Cu(II) ion due to the presence of another negatively charged ligand group (Qu-6-COO[−]) in **2**, while the other ligand groups in **1** are electrically neutral (2A4Pic).

4. Conclusions

The supramolecular structures of two highly symmetric 1D coordination polymers [Cd(2A4Pic)₂(N₃)₂]_n (**1**) and [Cu(Qu-6-COO)(N₃)(H₂O)]_n (**2**) were presented. Both complexes were assembled from the reaction of the organic ligand with the corresponding metal(II) nitrate in the presence of azide as a linker. The CdN₆ and CuN₂O₄ coordination spheres in complexes **1** and **2** have distorted octahedral configuration. In both complexes, the azide ligand has a μ(1,1) bridging mode. In addition, the Qu-6-COO[−] and water in complex **2** are connectors between the Cu(II) sites. Hirshfeld calculations revealed the 1D polymeric backbone of both complexes where the 1D backbone structures are interconnected by N...H H-bonds and π–π interactions. The N...H contacts are contributed by 43.1 and 27.4% in the molecular packing of **1** and **2**, respectively. In addition, the %C...C contacts are 5.6 and 9.3%, respectively. AIM analysis showed predominant closed-shell interactions for the Cd–N, Cu–N, and Cu–O coordinate bonds. Additionally, natural charge analysis sheds the light on the higher compensation of the central metal ion positive charge in **2** than in **1**.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/sym15030619/s1>, Chemicals and Physicochemical characterizations; Crystal structure analysis; DFT calculations; CheckCIF reports; Figure S1. The FP plots and d_{norm} surface maps for the N...H and H...H contacts in complex **1**; Figure S2. Shape index (SI; left) and curvedness (right) maps reveal the π–π stacking interactions in complex **1**; Figure S3. The FP plots and d_{norm} maps of the significant contacts in **2**; Figure S4. Red/blue triangles in SI map reveal the presence of π–π stacking interactions in complex **2**; Table S1. The %contacts in compounds **1** and **2**; Table S2 AIM parameters (a.u.) at BCPs for complexes **1** and **2**.

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