

Article

Coordination Polymers with a Pyrazine-2,5-diylldimethanol Linker: Supramolecular Networks through Hydrogen and Halogen Bonds

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Abstract: In this paper, the synthesis and crystal structure of pyrazine-2,5-diylldimethanol (pyzdmH2, C₆H₈N₂O₂), a new symmetric water-soluble N,O-chelating tetra-dentate organic ligand, is reported and an environmentally friendly method is used to synthesize coordination compounds in water under ambient conditions, from the reaction of pyzdmH2 with the halide salts of Cu(II), Zn(II), Hg(II) and Cd(II): {[Cu(pyzdmH2)_{0.5}(μ-Br)(Br)(H₂O)]·H₂O}_n **1**, {[Zn₂(pyzdmH2)(μ-Cl)(Cl)₃(H₂O)]·H₂O}_n **2**, [Hg₂(pyzdmH2)_{0.5}(μ-Cl)₂(Cl)₂]_n **3**, {[Cd₂(pyzdmH2)(μ-Cl)₄]·H₂O}_n **4**, and {[Cd₂(pyzdmH2)(μ-Br)₄]·H₂O}_n **5**. Single-crystal X-ray diffraction analysis reveals that **1–3** are 1D coordination polymers and **4** and **5** are 3D coordination networks, all constructed by bridging pyrazine-2,5-diylldimethanol and halogen ions. The hydroxyl groups in the organic linker extend the 1D chains to non-covalent 3D networks. In all non-covalent and covalent 3D networks, water molecules are trapped by strong hydrogen bond interactions. Supramolecular analysis reveals strong O-H···O, O-H···N, O-H···X, and weak C-H···O, C-H···X (X = Cl, Br) hydrogen bonds, as well as π-π(pyrazine ring), metal-halogen···π(pyrazine ring), and O-H···ring(5-membered chelate ring) interactions. In addition, X···O weak halogen bonds are present in **1–5** (X = Cl and Br).

Keywords: pyrazine-diylldimethanol; coordination polymers; hydrogen bonding interaction; halogen bonding interaction



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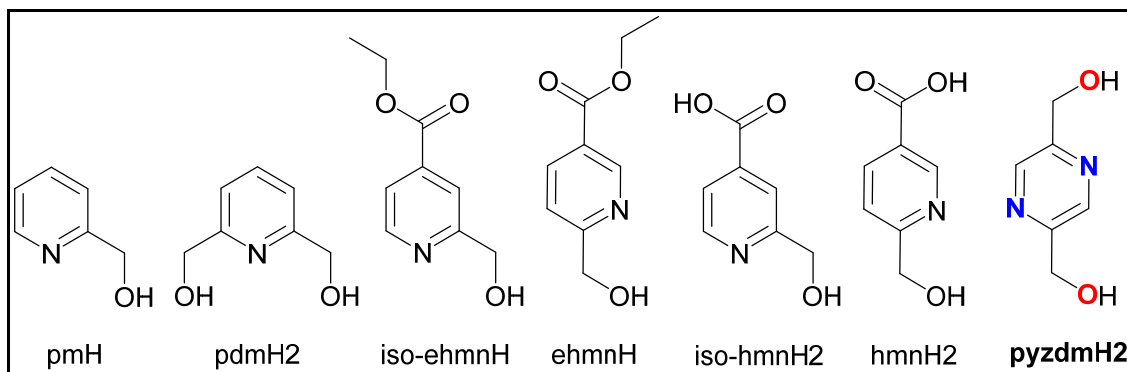


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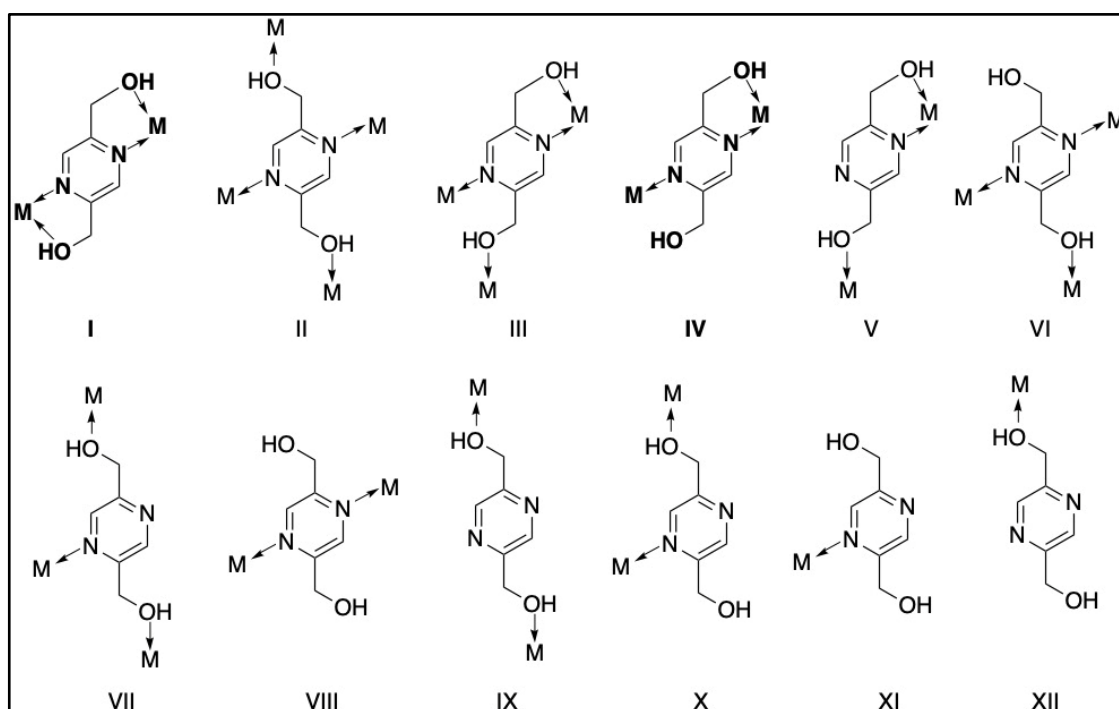
1. Introduction

Pyridine–alcohol based ligands are versatile N,O chelating organic linkers because of the rich σ donating and strong coordination toward a wide range of transition metal ions. This large number of structures directed us toward designing and synthesizing new polydentate multi-functional ligands, providing a hydroxyl group beside the nitrogen atom and a carboxylic acid group in a different position on the pyridine ring [1–3]. Our studies on 2-hydroxylmethylpyridine-carboxylate ligands (Scheme 1) showed that in mononuclear complexes, the pyridine alcohol group has a higher tendency towards coordination with the first row of transition metal ions than with the carboxylate group [4–7]. Therefore, we planned to extend our studies on pyrazine alcohols by synthesizing pyrazine-2,5-diylldimethanol (pyzdmH2) (Scheme 1) as a new organic linker and, we hypothesized, as the source of a large diversity of stable coordination compounds. Scheme 2 depicts the potential variety of pyzdmH2 coordination modes, which create different coordination geometries [8–10]. Despite being able to coordinate with the transition metal ions, pyzdmH2 can interact in several different ways. For example, both nitrogen atoms and the hydroxyl groups can be involved in hydrogen bonds. The pyrazine C–H can act as a weak hydrogen bond donor, and the pyrazine ring can be involved in various π-interactions [11–14]. Furthermore, considering that a pyrazine ring and alcohol groups can be part of biological

systems, coordination compounds assembled from pyrazine–diylldimethanol based ligands with biocompatible or non-biocompatible metals can be biologically important [15–17]. Moreover, pyzdmH2 is a symmetric water-soluble organic ligand and the high solubility of pyrazine’s alcohol-based ligands is important for their roles in biochemistry.



Scheme 1. Pyridine–alcohol based ligands and pyrazine-2,5-diylldimethanol (pyzdmH2).



Scheme 2. The possible coordination modes of pyrazine-2,5-diylldimethanol. **I** and **IV** have been observed in compounds 1–5.

This research first focused on the synthesis of pyrazine-2,5-diylldimethanol (pyzdmH2, $C_6H_8N_2O_2$) and then on the synthesis of coordination compounds assembled from pyzdmH2 and the first row or d^{10} transition metal elements by using metal halide salts as inorganic precursors [18,19]. The high water solubility of pyzdmH2 and the water soluble metal halide salts $CuBr_2$, $ZnCl_2$, $HgCl_2$, $CdCl_2 \cdot H_2O$, and $CdBr_2 \cdot 4H_2O$ allowed us to study the coordination modes of pyzdmH2 with $Cu(II)$, $Zn(II)$, $Hg(II)$, and $Cd(II)$ without using organic solvents, high temperature, or pressure. We hope that this approach will facilitate the synthesis of water-stable and cost-effective coordination compounds that can be easily scaled up in water.

2. Materials and Methods

Reagents were obtained from commercial sources and used without further purification. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III-300. IR spectra were recorded on a Bruker Tensor 37 IR spectrometer equipped with an ATR unit (Platinum ATR-QL, Diamond). Elemental analyses were conducted with a PerkinElmer CHN 2400 Analyzer. The powder X-ray diffraction patterns (PXRD) were obtained on a Bruker D2 Phaser powder diffractometer with a flat silicon, low background sample holder, at 30 kV, 10 mA for Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$).

2.1. Single X-ray Crystallography

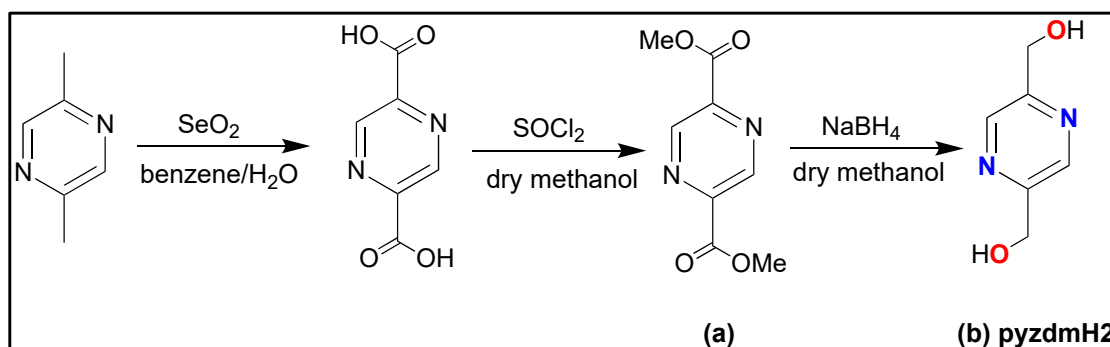
Suitable crystals were carefully selected under a polarizing microscope, covered in protective oil, and mounted on a cryo-loop. The single crystal X-ray diffraction measurements of pyzdmH2 and 1–5 were carried out on a Bruker Kappa APEX-II CCD diffractometer with Mo-K α radiation (microfocus tube, multi-layer mirror system, $\lambda = 0.71073 \text{ \AA}$) applying ϕ - and ω -scans at temperatures 140(2) and 296(2) K [20]. Evaluation of the crystal system, orientation matrix, and cell dimensions were carried out with the APEX4 software suite [20]. SMART, SAINT, and SADABS [21,22] were used for the calculations of data collection/unit cell refinement, frame integration/data reduction, and multi-scan absorption correction, respectively. XPREP (Sheldrick, 2008) was used to set up files for structure solutions. The structures were solved straightforwardly by direct methods (SHELX-97, XS and XT) and refined on F2 by full-matrix least-squares techniques with the SHELXTL and OLEX2-1.3 programs [23–25]. All non-hydrogen atoms in pyzdmH2 and 1–5 were refined anisotropically. All hydrogen atoms in pyzdmH2 and 1–5 were seen in the related Fourier maps after all non-hydrogen atoms were located. However, to achieve better data over parameters, H-atoms connected to $\text{C}_{\text{aromatic}}$ and $\text{C}_{\text{aliphatic}}$ were fixed at calculated positions using the riding model approximations on the atoms AFIX 43 and AFIX 23, respectively ($\text{C}_{\text{aromatic}}\text{—H}$ 0.930, and $\text{C}_{\text{aliphatic}}\text{—H}$ 0.970 $\text{\AA}$, as the values for room temperature, and $\text{C}_{\text{aromatic}}\text{—H}$ 0.950 $\text{\AA}$, $\text{C}_{\text{aliphatic}}\text{—H}$ 0.990, $\text{\AA}$ the values for 140 K, with $U(\text{H})$ set to $1.2U(\text{C})$). All the hydrogen atom positions of the hydroxyl groups of pyzdmH2 and coordinated and non-coordinated water molecules were assigned by difference Fourier calculations, with SHELXL-2017 and OLEX2-1.3 [25,26], and then refined with $U(\text{H})$ set to $1.5U(\text{O})$. The detailed structural refinement, including the applied restraint and constraint for pyzdmH2 and 1–5, are given in the supplementary information. The crystallographic data and structural refinement results along with further details of data collections and analyses are listed in Table S1 (Supporting Information). Molecular graphics were drawn with 3D visualized software Diamond version 4.6.8. and Mercury version 206425. [27–30].

2.2. Synthetic Procedures for pyzdmH2

2.2.1. Preparation of Dimethyl Pyrazine-2,5-dicarboxylate (a in Scheme 3)

Synthesis of dimethyl pyrazine-2,5-dicarboxylate is undertaken in two steps (Scheme 3) [2,3]. The first step is the oxidation of 2,5-dimethylpyrazine (9.9 g, 91.70 mmol) using selenium dioxide (49.50 g, 446.10 mmol) by reflux in a 10:1 pyridine/water mixture overnight. The hot mixture is filtered to remove the bulk of the elemental selenium produced and then evaporated to dryness. The crude pyrazine-2,5-dicarboxylic acid is then esterified using thionylchloride (7.02 g, 58.98 mmol) in methanol by refluxing overnight. Dimethylpyrazine-2,5-dicarboxylate (a in Scheme 3) is isolated as analytically pure crystals in 40% yield from 2,5-dimethylpyrazine by slow evaporation from methanol. Collected as an orange solid, the yield was $\sim$ (5 g, 40%). Melting point 164°C , selected IR data (cm^{-1}), (KBr pellet): 3424 (m), 3076 (s) ($\text{C-H}_{\text{aromatic}}$), 3016 (w) ($\text{C-H}_{\text{aromatic}}$), 2960 (m) ($\text{C-H}_{\text{aliphatic}}$), 2853 (w) ($\text{C-H}_{\text{aliphatic}}$), 1720 (vs) (C=O), 1541 (w), 1472 (m), 1433 (s), 1359 (s), 1278 (vs) (O-Me), 1202 (w), 1182 (m), 1143 (s) (O-Me), 1019 (s) (O-Me), 958 (m), 822 (m), 757 (s), 679 (w), 493 (w), 465 (m), 424 (m) cm^{-1} . MS (EI, 80°C , m/z): 196 [M]. Anal. calcd (solvent-free): (%) for $\text{C}_8\text{H}_8\text{N}_2\text{O}_4$ (169.16 g/mol): C 48.98, H 4.11, N 14.28; found: C 48.31, H 4.54, N 14.97%. ^1H NMR (300 MHz, CDCl_3) δ : 9.33 (s, 2H, pyzH), 4.22 (s, 6H, CH_3) ppm (Figure S1). ^{13}C [^1H]

NMR (75 MHz, CDCl_3) δ : 163.5 (pyzCO), 145.5 (pyzH), 145.3 (pyzH), 53.5 (OCH_3) ppm (Figure S2).



Scheme 3. Synthesis of pyzdmH2.

2.2.2. Preparation of Pyrazine-2,5-diylldimethanol (b in Scheme 3)

To a yellowish methanol solution (50 mL) containing dimethyl pyrazine-2,5-dicarboxylate (2.0 g, 10.2 mmol), NaBH_4 (3.1 g, 81.95 mmol) was slowly added at 0°C while stirring under inter atmosphere. After the addition was completed, the mixture was stirred for 3 h at room temperature overnight. The reaction was quenched by dropwise addition of H_2O . The resulting dark precipitate was filtered off, followed by solvent evaporation. Liquid–liquid extraction of the resulting mixture with CHCl_3 and H_2O continued for two days, followed by solvent evaporation, which gave a colorless single crystal of pyrazine-2,5-diylldimethanol (0.5 g, 35%). The long extraction is necessary as the pyrazine-2,5-diylldimethanol formed is very soluble in water. The obtained crystals of pyzdmH2 were stored in the mother liquor until single crystal analysis. Melting point $77\text{--}80^\circ\text{C}$, selected IR data (cm^{-1}), (KBr pellet): 3320 (b) ($\text{O-H}_{\text{alcohol}}$), 2920(w), 2832 (w) ($\text{C-H}_{\text{aliphatic}}$), 1490 (m), 1444 (s), 1351 (s), 1286 (m), 1220 (w), 1153 (m), 1063 (vs), 1022 (s), 911 (w), 873 (w), 783 (w), 732 (m), 669 (m), 604 (m), 529 (w), 451 (w). MS (EI, 60°C): 140 m/z : 140 [M], 139 [M-H]. Anal. calcd (solvent-free): (%) for $\text{C}_6\text{H}_8\text{N}_2\text{O}_2$ (140.14 g/mol): C 51.42, H 5.75, N 19.99; found: C 51.49, H 5.52, N 19.51. ^1H NMR (300 MHz, Acetone- d_6) δ : 8.51 (s, 2H, pyzH), 4.64 (s, OH), 4.62 (s, 4H, CH_2), 4.50 (t, J 2 Hz, OH) ppm (Figure S3). ^{13}C {1H} NMR (101 MHz, Acetone- d_6): d 155.8 (pyzCH2), 142.1 (pyz), 64.0 (CH_2) ppm (Figure S4).

2.3. Syntheses of 1–5

Water solutions of CuBr_2 (2.67 mg, 0.048 mmol), ZnCl_2 (9.81 mg, 0.072 mmol), HgCl_2 (19.37 mg, 0.072 mmol), $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ (4.36 mg, 0.024 mmol), $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ (8.18 mg, 0.024 mmol), and pyrazine-2,5-diylldimethanol (3.33 mg, 0.024 mmol) were mixed in H_2O (3 mL) in glass tubes to give greenish, colorless, colorless, colorless, and yellowish solutions respectively. The solutions were placed on top of water in an ultrasonic bath overnight at room temperature. The block-shaped crystals of 1–5 were obtained by slow evaporation of water over several weeks at room temperature, with a yield of 32%, 56%, 42% 63%, and 59%, respectively. Anal. calcd: (%) for $\text{C}_6\text{H}_{12}\text{Cl}_4\text{N}_2\text{O}_4\text{Zn}_2$ (2): C 16.06, H 2.70, N 6.24; found: C 16.65, H 3.09, N 6.37. Anal. calcd: (%) for $\text{C}_6\text{H}_8\text{Cl}_4\text{Hg}_2\text{N}_2\text{O}_2$ (3): C 10.55, H 1.18, N 4.10; found: C 10.78, H 1.20, N 4.39. Anal. calcd: (%) for $\text{C}_6\text{H}_{10}\text{Br}_4\text{Cd}_2\text{N}_2\text{O}_3$ (5) (%): C 10.26, H 1.43, N 3.99; found: C 10.64, H 1.54, N 4.17. The obtained crystals were stored in the mother liquor until single crystal analysis. During the X-ray data collection, several single crystals from one batch were randomly selected and measured to determine their unit cell dimensions and, consequently, assess the phase purity. All of the crystals exhibited identical unit cell dimensions.

3. Result and Discussion

3.1. Synthesis of Organic Linker and Coordination Polymers

To explore and understand the diverse coordination modes of pyzdmH2 to Cu(II), Zn(II), Hg(II), and Cd(II), and their role on the crystal structure design, herein we describe the crystal structure of pyzdmH2 and 1–5. The coordination modes I and IV in Scheme 2 have been observed in 1–5. In this research, the most conventional non-covalent interactions (NCIs), hydrogen bonds, π - π stacking, and halogen bond interactions as the main stabilizing forces in supramolecular structure, as well as possible 3D covalent network formation, have been widely investigated [31–33]. Furthermore, other secondary bonding interactions (SBIs), like oxygen–oxygen interaction, which may also play a considerable role in supramolecular interactions or crystal structure design, have been surveyed [34–37].

Based upon the previous successful synthesis of a series of functionalized 2-hydroxymethyl pyridine carboxylate esters or carboxylic acids [2,3], pyzdmH2 has been synthesized in three steps (Scheme 3). This comprised the oxidation of 2,5-dimethylpyrazine by selenium dioxide, followed by the esterification and then the reduction of dimethyl pyrazine-2,5-dicarboxylate. The pure product, pyzdmH2, was obtained after purification by crystallization.

By using aqueous solutions of CuBr₂, ZnCl₂, HgCl₂, CdCl₂·H₂O, and CdBr₂·4H₂O with an aqueous solution of pyzdmH2 under ambient conditions in an ultrasonic bath, five new coordination polymers 1–5 were synthesized and isolated in the single-crystal solid phase. The molar ratios of CuBr₂, ZnCl₂, HgCl₂, CdCl₂·H₂O, and CdBr₂·4H₂O to pyzdmH2 were kept at 1:2, 1:3, 1:3, 1:1, and 1:1 for preparing 1–5, respectively. Single crystals of compounds 1–5 were grown in an aqueous solution. The compounds {[Cu(pyzdmH2)_{0.5}(μ-Br)(Br)(H₂O)]·H₂O}_n 1, {[Zn₂(pyzdmH2)(μ-Cl)(Cl)₃(H₂O)]·H₂O}_n 2, [Hg₂(pyzdmH2)_{0.5}(μ-Cl)₂(Cl)₂]_n 3, {[Cd₂(pyzdmH2)(μ-Cl)₄](H₂O)_n 4, and {[Cd₂(pyzdmH2)(μ-Br)₄](H₂O)_n 5 were derived from single-crystal X-ray structure analyses. Compounds 1–3 feature 1D polymeric structures constructed from μ₂-halide, μ₂-pyzdmH2 and double μ₂-halide (Scheme 4). Cd²⁺ compounds 4 and 5 feature 3D network structures that are also constructed from double μ₂-halide and μ₂-pyzdmH2 (Scheme 5). In all compounds, except for 3, pyzdmH2 functions as a tetra-dentate linker that forms two chelate rings (model I in Scheme 2). However, in 3, one of the hydroxyl groups of pyzdmH2 functions as a side arm, resulting in a tri-dentate linker (model IV in Scheme 2). We observed that water molecules and the hydroxyl groups from pyzdmH2 have key roles in the formation of the 3D non-covalent and covalent networks of compounds 1–5, due to the strong hydrogen bond interactions present within these structures. The key hydrogen bond interactions are listed in Table 1.

Table 1. Key hydrogen bond interactions for pyzdmH2 and 1–5 [Å and °] with standard uncertainties in parentheses.

D-H...A	d(D-H)	d(H...A) ^(a)	d(D...A) ^(a)	<(DHA) ^(b)
pyzdmH2				
O(1)-H(1)···N(2)	0.87(16)	1.97(16)	2.84(12)	171
O(2)-H(2)···O(3)#iii	0.85(16)	1.87(16)	2.72(11)	174
O(3)-H(3)···N(3)#ii	0.85(16)	1.99(16)	2.80(11)	159
Symmetry transformations used to generate equivalent atoms: ii = −x + 2, −y + 2, −z + 1 #iii = x, −y + 3/2, z − 1/2.				
1				
O(1)-H(1)···O(2)#iii	0.82(16)	1.82(2)	2.63(18)	172
O(2)-H(2A)···O(3)#iv	0.82(2)	1.96(2)	2.77(21)	173
O(2)-H(2B)···O(3)#iii	0.78(2)	2.06(2)	2.83(20)	169
O(3)-H(3A)···Br(1)#v	0.87(2)	2.55(2)	3.23(16)	135
O(3)-H(3B)···Br(2)#vi	0.80(2)	2.49(2)	3.29(15)	178
Symmetry transformations used to generate equivalent atoms: iii = 1 − x, 1 − y, 1 − z, iv = 1 − x, −1/2 + y, 1/2 − z, v = 1 − x, −1/2 + y, 1/2 − z, vi = 1 − x, 1 − y, −z.				

Table 1. Cont.

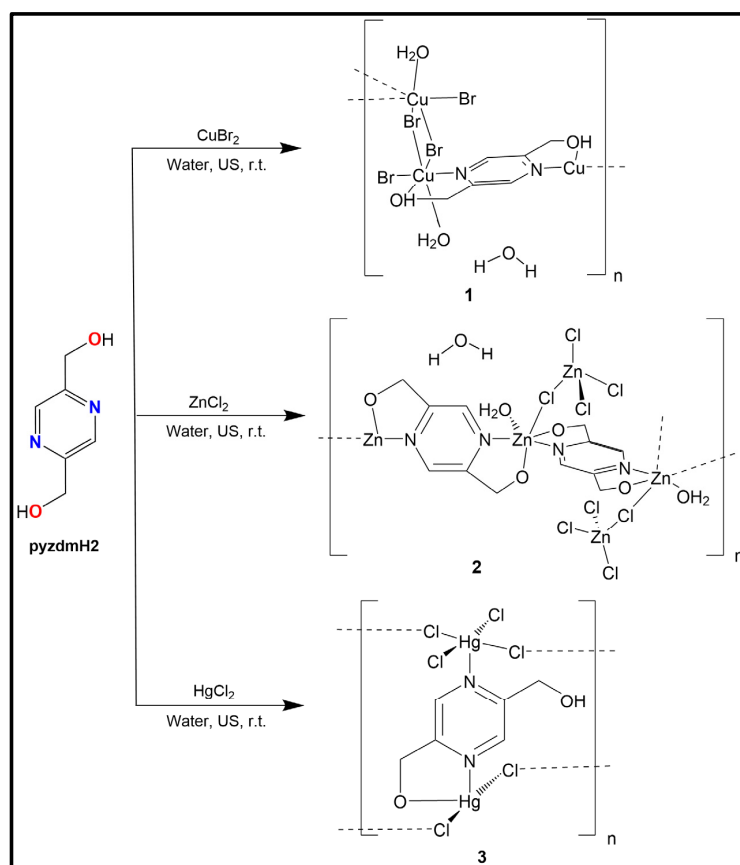
D-H...A	d(D-H)	d(H...A) ^(a)	d(D...A) ^(a)	<(DHA) ^(b)
2				
O(1)-H(1)···O(4)#iii	0.87(2)	1.72(2)	2.59(3)	175
O(2)-H(2)···Cl(2)#iv	0.83(3)	2.25(3)	3.08(19)	176
O(3)-H(3B)···Cl(3)#iv	0.82(4)	2.38(4)	3.16(2)	160
O(3)-H(3A)···Cl(4)#v	0.82(4)	2.29(4)	3.10(2)	170
O(4)-H(4A)···Cl(4)	0.85(3)	2.38(3)	3.16(2)	153
O(4)-H(4B)···Cl(2)	0.84(3)	2.55(4)	3.29(2)	148
Symmetry transformations used to generate equivalent atoms: iii = x − 1, y, z, iv = x − 1/2, −y + 3/2, z + 1/2, v = −x + 1/2, y + 1/2, −z + 1/2.				
3				
Intra O(1)-H(1)···O(2)#i	0.82(19)	1.93(2)	2.73(3)	165
Intra O(1)-H(1)···Cl(4)#i	0.82(19)	2.75(2)	3.12(3)	109
O(2)-H(2)···O(1)#iii	0.83(19)	2.25(3)	2.96(3)	143
O(2)-H(2)···Cl(2)#iii	0.83(19)	2.82(4)	3.45(3)	136
Symmetry transformations used to generate equivalent atoms: i = −x + 2, −y + 1, −z + 1, iii = x, y, z − 1.				
4				
O(1)-H(1A)···O(2)#x	0.85(6)	1.83(10)	2.62(10)	154
O(1)-H(1A)···O(2)#iv	0.85(6)	1.99(10)	2.69(10)	138
O(1)-H(1B)···O(1)#iv	0.85(8)	1.82(10)	2.62(5)	156
O(2)-H(2B)···O(1)#iv	0.93	1.85	2.69(10)	149
O(2)-H(2A)···Cl(2)#ii	0.80	2.65(13)	3.26(9)	134
O(2)-H(2A)···Cl(2)#v	0.80	2.68(13)	3.18(9)	122
Symmetry transformations used to generate equivalent atoms: ii = −x + 1, −y + 1, −z + 1, iv = −x + 1, −y, −z + 1, v = x, 1 − y, 1/2 + z, x = x, −y, z − 1/2.				
5				
O(1)-H(1A)#vi···O(2)	0.85(6)	1.83(7)	2.68(10)	172(8)
O(1)-H(1B)#v···O(1)#ii	0.85(6)	1.81(9)	2.64(5)	165(12)
O(2)-H(2B)···O(1)#v	0.72	1.99	2.70(10)	165
O(2)-H(2A)···Br(2)	0.84	2.78	3.39(9)	131
O(2)-H(2A)···Br(2)#i	0.84	2.88	3.33(9)	115
Symmetry transformations used to generate equivalent atoms: i = −x + 1, y, −z + 3/2, ii = −x + 1, −y + 1, −z + 1, v = x, y + 1, z, vi = 1 − x, y + 1, 3/2 − z.				

^(a) The hydrogen bond lengths highlighted in bold indicate hydrogen bonds that are typically between 0.45 and 0.20 Å shorter than the sum of the van der Waals radii of the atoms participating in the hydrogen bond. ^(b) The bond angles highlighted in bold indicate angles that are within 5° to 180°.

3.1.1. Crystal Structure of Pyrazine-2,5-diylldimethanol (pyzdmH2)

Pyrazine-2,5-diylldimethanol (pyzdmH2) crystallizes in the monoclinic centrosymmetric $P2_1/c$ space group (Table S1). The atoms of one and a half formula units in general positions define the asymmetric unit of the crystal structure in pyzdmH2 ($Z = 6$, $Z' = 1.5$). Figure 1 shows the atomic displacement ellipsoids for the asymmetric unit, and the atomic numbering in this compound. As shown, one molecule is located on a crystallographic inversion center. Selected bond lengths, angles, and torsion angles are summarized in Table S2. PyzdmH2 crystallizes in two different conformations with regard to the dangling methanol groups (H_2C-OH). The methanol groups O1-H1, O2-H2, and O3-H3 are not coplanar with the attached pyrazine rings in the both conformations, and are twisted with respect to the mean plane of the pyrazine rings by 135.14(1), 147.86(1), and 95.00(2)°, respectively, and $\angle O1-H1-C1-C2$, $\angle O1^i-H1^i-C1^i-C2^i$, $\angle O2-H2-C4-C5$, and $\angle O3-H3-C9-C8$ torsion angles are 134.8, −134.8, 155.3, 78.8°, respectively (see Table S2 for symmetry codes). In the crystal structure, the molecules pack in a one-dimensional strand-like arrangement generated by pyzdmH2 molecules of the same conformation (N2-C5-C6-N3-C8-C7) along the crystallographic c -axis. The adjacent pyzdmH2 molecules are connected in a side-by-side arrangement along the crystallographic c -axis through a strong hydrogen bond O2-H2···O3ⁱⁱⁱ to generate the one-dimensional strands with an intermolecular separation

of 1.87(16) Å. These strands are sewn to the neighboring strands by the hydrogen bonds $O3-H3\cdots N3^{ii}$ with an intermolecular separation of 1.99(16) Å and are further sewn with the aid of pyzdmH2 molecules, which contain the pyrazine ring that is generated by a crystallographic inversion center via a hydrogen bond $O1-H1\cdots N2$ with intermolecular separation 1.97(16) Å (Figure 2a). These strong hydrogen bonds may play key role in directing the configuration of pyzdmH2 in the single crystal structure (Table 1). PyzdmH2 molecules from the same conformations are further stacked via hydrogen bonds $C1-H1A\cdots O1^v$, $C4-H4B\cdots O2^{iv}$, and $C9-H9A\cdots O3^v$ (Figure 2b, Table S3), in such a manner that there are no strong π - π interactions between pyrazine rings (centroid $\cdots$ centroid distance 4.06 Å, Figure S5a, Table S4) [38]. One view of the crystal packing is depicted in Figure S5b.



Scheme 4. Schematic presentation of the synthesis of 1–3.

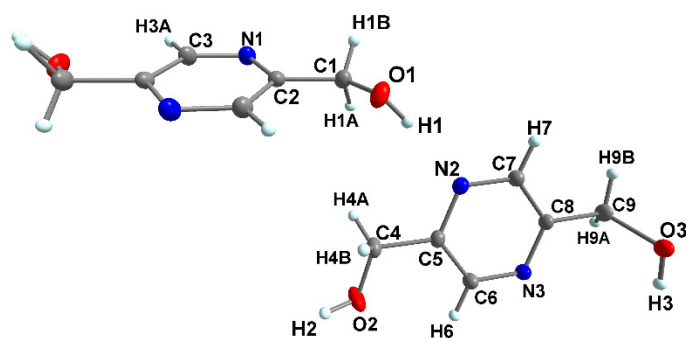
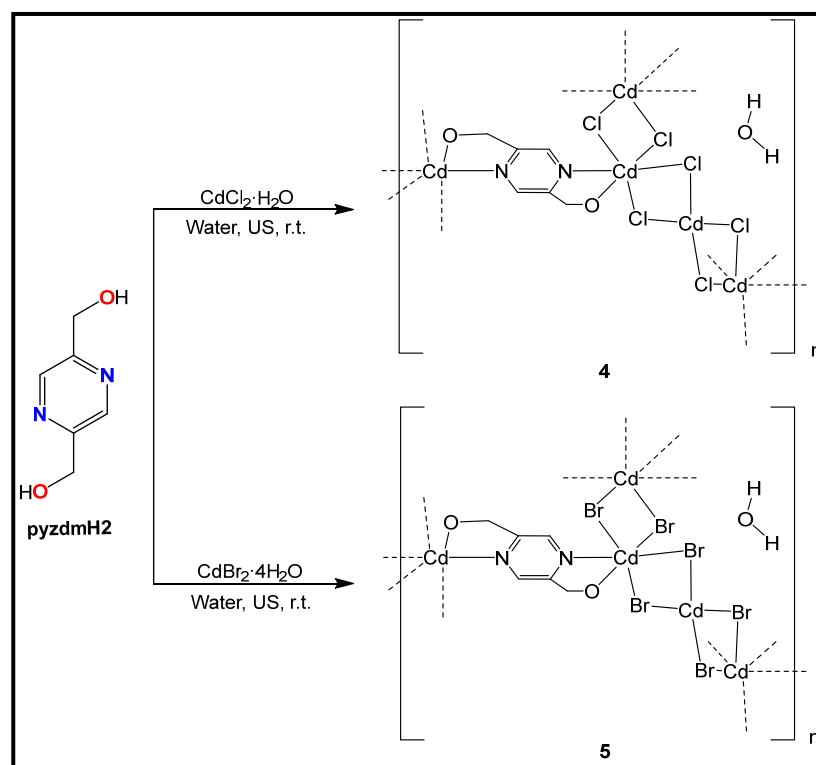


Figure 1. Expanded asymmetric unit of pyzdmH2 along with the atom labelling scheme. For the sake of clarity, hydrogen bonds are omitted. Displacement ellipsoids are drawn at the 50% probability level and H atoms are of arbitrary radii. Unlabeled atoms are generated by the symmetry operation $i = 1 - x, 1 - y, -z$.



Scheme 5. Schematic presentation of the synthesis of 4 and 5.

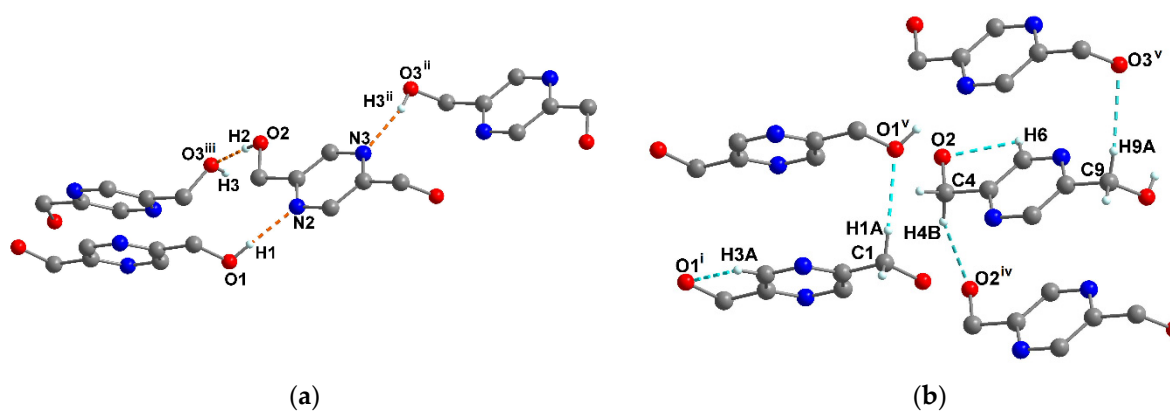


Figure 2. (a) Hydrogen bonds of the O-H...O and O-H...N types are depicted by dashed bonds in orange. (b) Hydrogen bonds of the C-H...O type are depicted by dashed bonds in turquoise blue. Symmetry codes: $i = 1 - x, 1 - y, -z$ $\#ii = -x + 2, -y + 2, -z + 1$ $\#iii = x, -y + 3/2, z - 1/2$ $\#iv = x, -1 + y, z$ $\#v = x, 1 + y, z$.

3.1.2. Crystal Structure of $\{[\text{Cu}(\text{pyzdmH2})_{0.5}(\mu\text{-Br})(\text{Br})(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ (**1**)

Compound **1** crystallizes in the monoclinic centrosymmetric space group $P2_1/c$ (Table S1). It is a 1D neutral coordination polymer, in which the Cu^{2+} ion is six-coordinated. The asymmetric unit of the polymeric structure contains one copper ion (Cu^{2+}), half of pyzdmH2, which forms a bridging tetra-dentate linker, two bromine ions, which are coordinated to the copper ion as terminal (Br2) and bridging (Br1) ligands, a coordinated water molecule (aqua ligand) (O2H2AH2B), and a non-coordinated water molecule (O3H3AH3B). All atoms are in general positions ($Z = 4$, $Z' = 1$). The 2+ charge on Cu is balanced by the bridging and terminal bromine ions. Figure 3 shows the atomic displacement ellipsoids for the asymmetric unit, along with the atomic numbering in **1**. The Cu^{2+} ion in the polymeric structure **1** is surrounded by the N and O atoms from pyzdmH2 in a chelating configuration, which are bonded at a relatively short distance from the central Cu^{2+}

ion [Cu–O1 = 1.9968(12), Cu–N1 = 2.0281(13) Å], two symmetry-related bridging bromine atoms in a *cis*-configuration [Cu–Br1 = 2.4112(3), and Cu–Br1ⁱⁱ = 3.0672(3) Å], one terminal bromine atom [Cu–Br2 = 2.3627(3) Å], and, finally, an O atom from the coordinated water molecule [Cu–O = 2.6590(15) Å]. This coordination environment forms a Jahn–Teller distorted tetragonal geometry around the d⁹ Cu²⁺ ion. The chelating N and O atoms from pyzdmH2, the terminal bromine atom (Br2) *trans* to the N atom, and one of the bridging Br atoms (Br1) *trans* to the O atom fill the equatorial plane. The axial positions are occupied by the coordinated water molecule and the symmetry-related bridging bromine atom to Br1. The five-membered chelate ring, Cg(2) = Cu–O1–C1–C2–N1, with a bite distance of 2.587 Å, deviates with the angle O1–Cu–N1 from 90° by about 10° and, subsequently, the angles ∠N1–Cu–Br1, ∠Br1–Cu–Br2, and ∠O1–Cu–Br2 deviate by about 6.4°, 5.3°, and 2°, respectively [39]. Selected bond distances, angles, and torsion angles of **1** are summarized in Table S2.

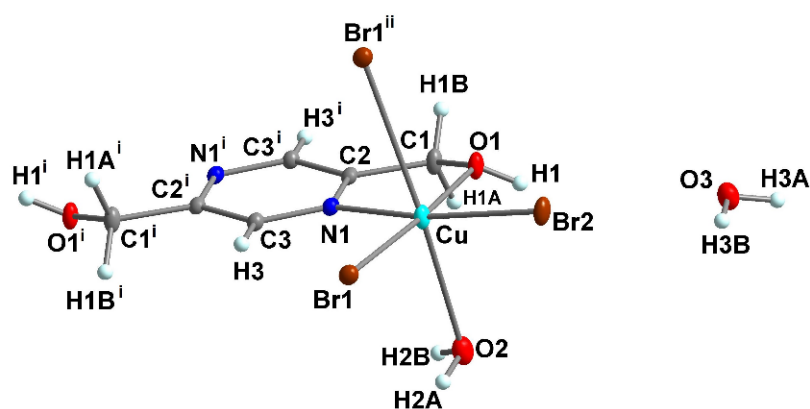


Figure 3. Asymmetric unit of **1** with the full coordination environment around Cu²⁺ along with the atom labelling scheme. The atoms defining the asymmetric unit are indicated without symmetry codes, showing displacement ellipsoids at the 50% probability level; H atoms are of arbitrary radii. Symmetry codes: i = 2 – x, 1 – y, 2 – z, and ii = 2 – x, 1 – y, 1 – z.

Each Cu²⁺ center connects to two adjacent Cu²⁺ centers through a pair of the bridging bromine atoms (Cu...Cu 3.99(4) Å) and through the tetra-dentate bridging pyzdmH2 linker (Cu...Cu 6.80(4) Å) to generate a one-dimensional stair-like chain structure, which extends along the crystallographic *c*-axis (Figure 4a). At the center of the four-membered Br1–Cu–Br1ⁱⁱ–Cuⁱⁱ lies a crystallographic inversion center, which renders this ring planar by symmetry (∠Cu–Br1ⁱⁱ–Cuⁱⁱ = 92.78(9)°). Adjacent chains are connected by strong hydrogen bonds between the OH groups of pyzdmH2 in one chain and O atoms from the coordinated water molecules in the neighboring symmetry-related chain [O1–H1...O2ⁱⁱⁱ = 1.82(2) Å] to form a supramolecular 2D sheet, which extends within the *ac* plane (Figure 4b, see Table S2 for symmetry codes). The coordinated water molecule connects to two symmetry-related crystal water molecules through two strong hydrogen bonds: O2–H2A...O3^{iv} and O2–H2B...O3ⁱⁱⁱ. Furthermore, the non-coordinated water molecule is involved in two hydrogen bonds: O3–H3A...Br1^v and O3–H3B...Br2^{vi} (Figure 4c, Table 1). The last four hydrogen bonds link the adjacent 2D sheets to extend a 3D non-covalent network along the *b*-axis (Figure 5a). The one-dimensional chains and 2D sheets are further linked through the longer hydrogen and halogen bond interactions listed in the Tables S5 and S7. In addition, there are short inter-chain interactions O–H...ring (5-membered chelate ring) (Table S6) [40]. There are no π – π (pyrazine ring) interactions in the crystal structure of **1**. Figure 5b shows the crystal-packing diagram of **1** with the unit cell.

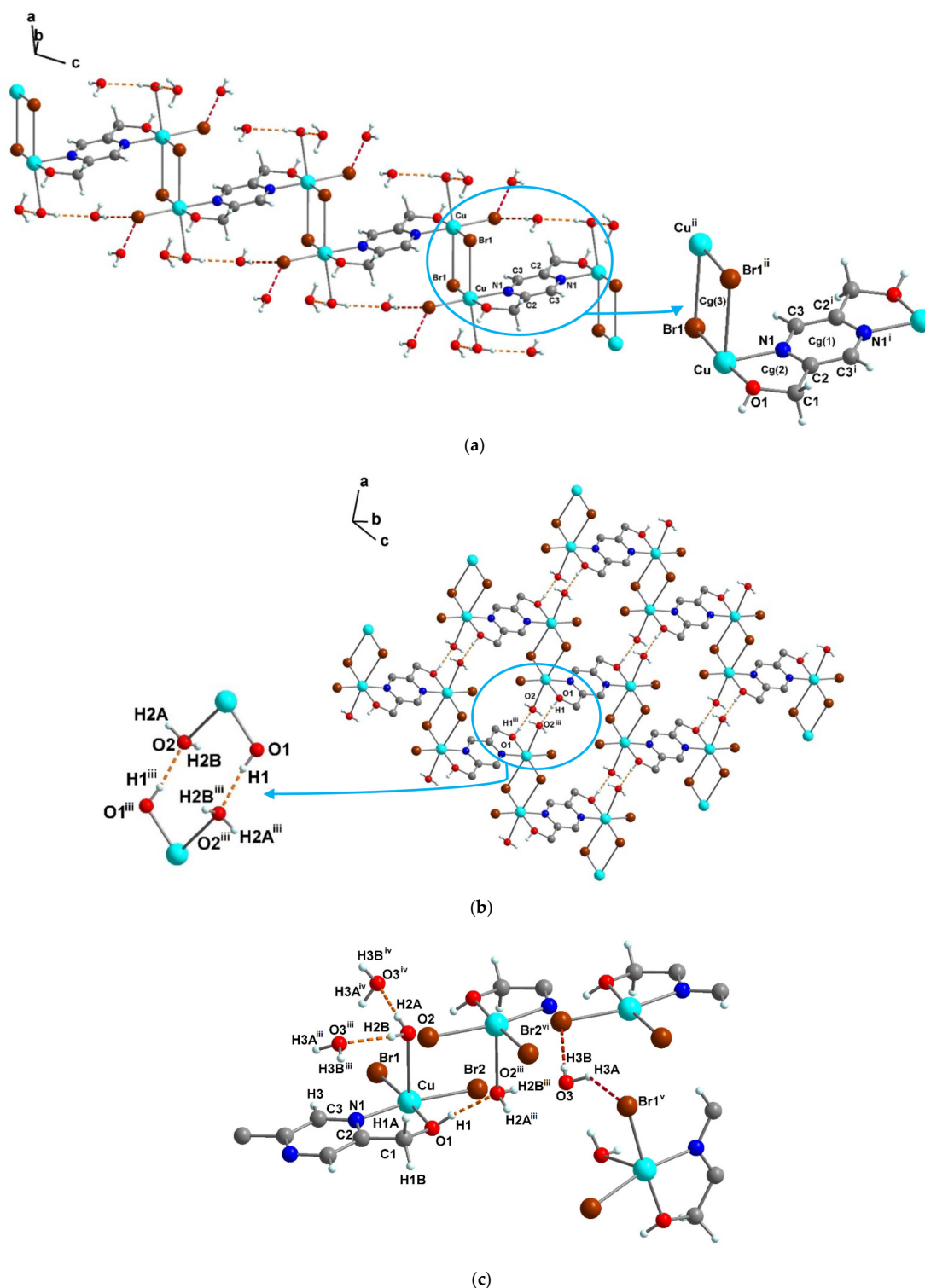


Figure 4. (a) One-dimensional stair-like chain in the structure of 1 along with the magnified depiction of Cg(1), Cg(2), and Cg(3). (b) A view of the 2D sheet created by the O1-H1...O2 hydrogen bond in the ac plane, depicted by dashed bonds in orange. For the sake of clarity, only the hydrogen atoms from the coordinated water molecule and the hydroxyl group from pyzdmH₂ are shown. (c) Hydrogen bonds O-H...O and O-H...Br are depicted by dashed bonds in orange and brick red, respectively. Symmetry codes: i = 2 - x, 1 - y, 2 - z, ii = 2 - x, 1 - y, 1 - z, iii = 1 - x, 1 - y, 1 - z, iv = 1 - x, -1/2 + y, 1/2 - z, v = 1 - x, 1/2 + y, 1/2 - z, vi = 1 - x, 1 - y, -z.

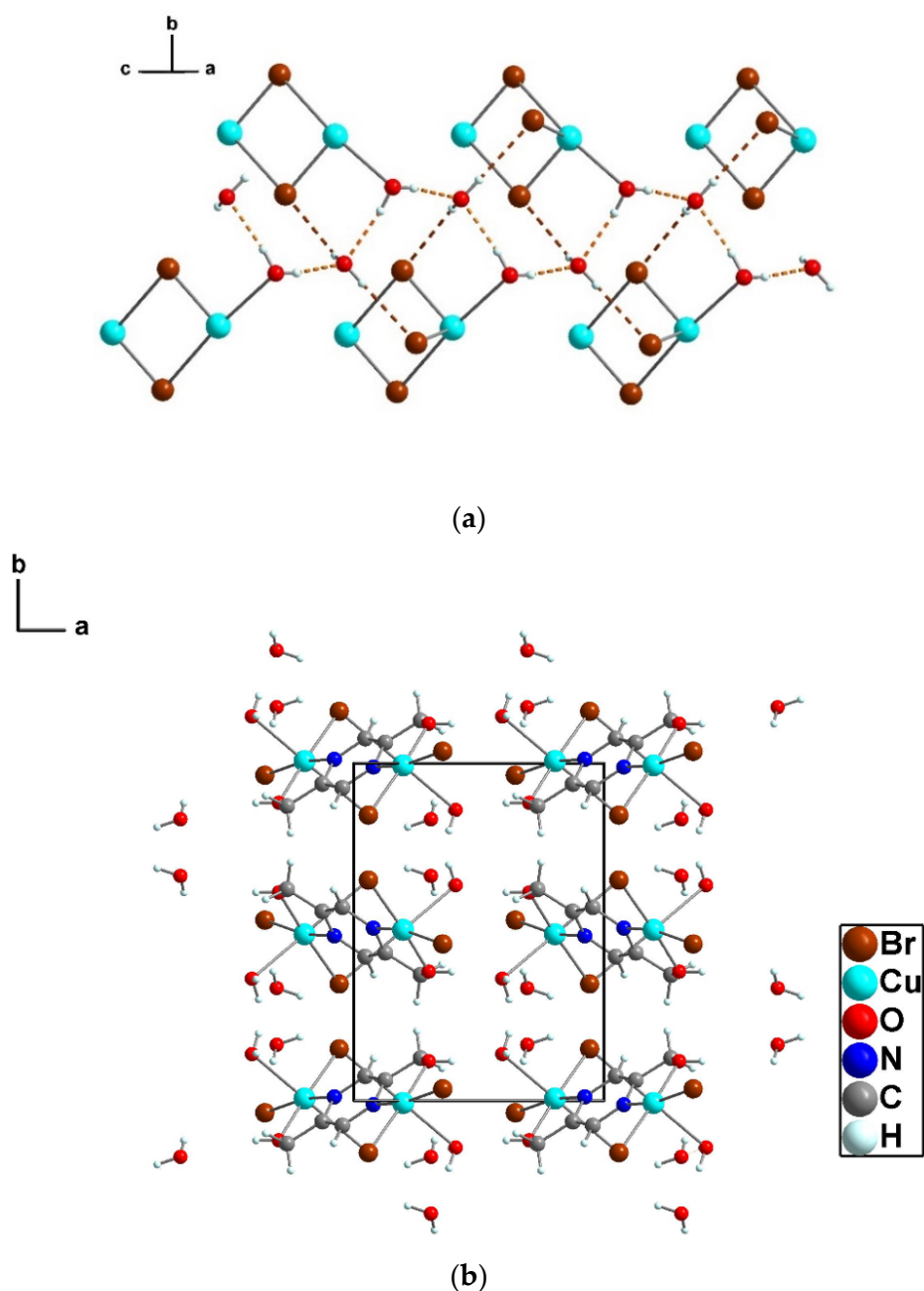


Figure 5. (a) Hydrogen bond network between the non-covalent 2D-sheets along the *b*-axis. (b) Cell packing diagram of 1 viewed along the *c*-axis with the color codes.

3.1.3. Crystal Structure of $[[\text{Zn}_2(\text{pyzdmH}_2)(\mu\text{-Cl})(\text{Cl})_3(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}]_n$ (2)

Compound 2 crystallizes in the centrosymmetric monoclinic space group $P2_1/n$ (Table S1) as a 1D neutral coordination polymer. The asymmetric unit contains two independent zinc ions (Zn1 and Zn2), one bridging the tetra-dentate pyzdmH2 linker between two symmetry-related zinc ions (Zn1, Zn1¹) and one bridging the chloride ion (Cl1), which coordinates with two independent zinc ions (Zn1 and Zn2), three terminal chloride ions (Cl2, Cl3, Cl4) coordinated with Zn2, a coordinated water molecule (O3H3BH3A), and a non-coordinated crystal water molecule (O4H4AH4B). All atoms are in general positions ($Z = 4$, $Z' = 1$). Figure 6a shows the atomic displacement ellipsoids for the asymmetric unit in 2, along with the atomic numbering.

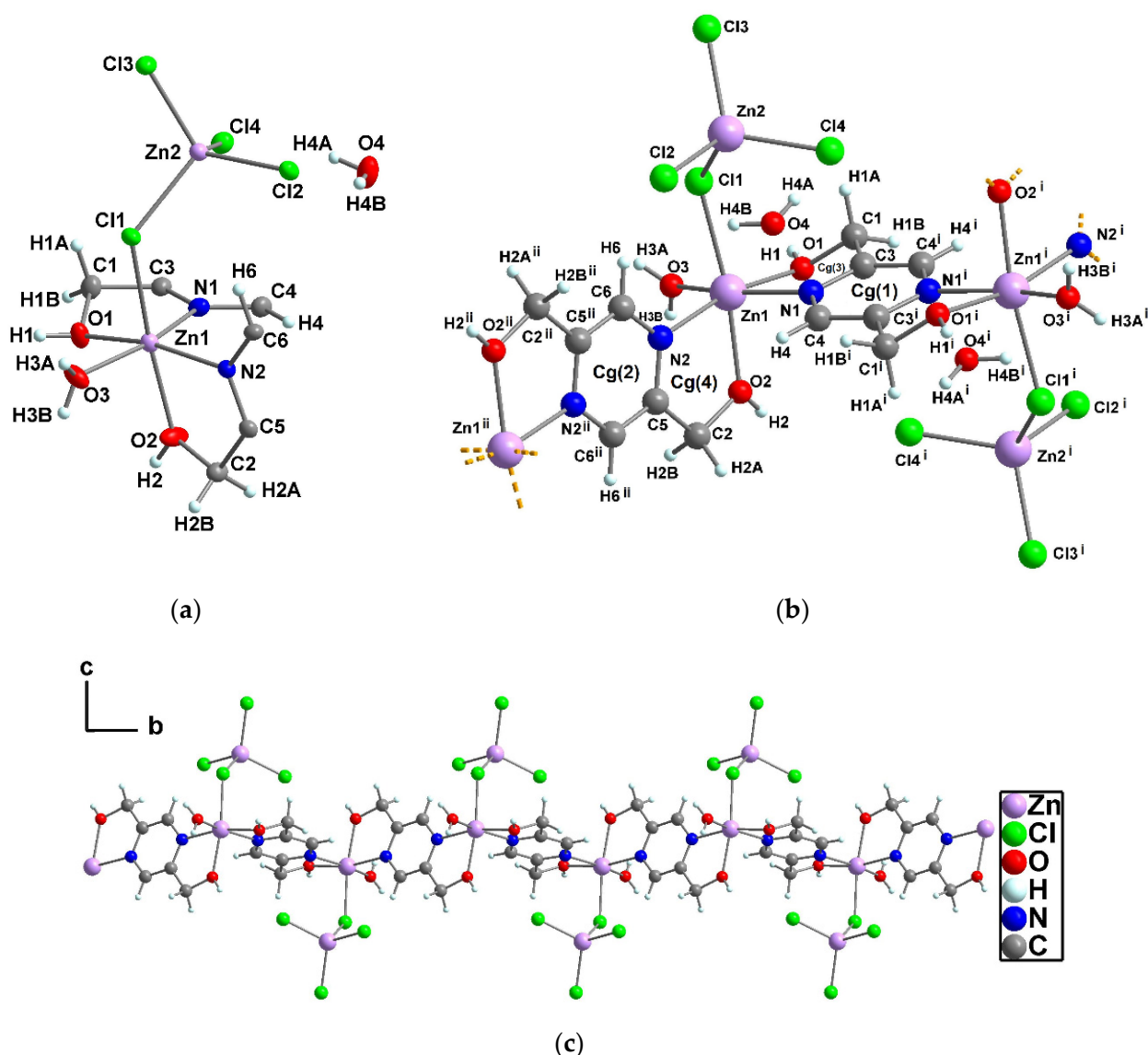


Figure 6. (a) Asymmetric unit of **2** along with the atom labeling scheme, showing displacement ellipsoids at a 50% probability level; H atoms are of arbitrary radii and, for the sake of clarity, hydrogen bonds are omitted. (b) Ball and stick presentation of the spatial full coordination environment around Zn1 and Zn2 in **2**. (c) One-dimensional polymeric zig-zag chain structure in **2** along the *b* axis with color codes. Symmetry codes: *i* = 1 − *x*, 1 − *y*, 1 − *z*, *ii* = 1 − *x*, 2 − *y*, 1 − *z*. Cg(1) = N1–C3–C4^{*i*}–N1^{*i*}–C3^{*i*}–C4, Cg(2) = N2–C5–C6^{*ii*}–N2^{*ii*}–C5^{*ii*}–C6, Cg(3) = Zn1–O1–C1–C3–N1, Cg(4) = Zn1–O2–C2–C5–N2.

The structure of **2** contains two kinds of coordination geometries around the Zn²⁺ ions, a six-coordinated Zn1 in a distorted octahedral geometry, and a four-coordinated Zn2 in an almost tetrahedral geometry (Zn2) (Figure 6b). The distorted octahedral Zn1 is defined by two chelating pyzdmH2 [Zn1–O1 = 2.0972(17), Zn1–N1 = 2.112(2), Zn1–O2 = 2.1259(18), Zn1–N2 = 2.1451(19) Å], an O atom from the coordinated water molecule [Zn1–O3 = 2.0447(18) Å], and the bridging chlorine (Cl1) from the tetrachloridozincate complex [Zn(2)Cl₄]^{2−} [Zn1–Cl1 = 2.4669(6) Å]. It should also be notable that the nitrogen atoms from the two pyzdmH2 chelators (N1, N2) are in *trans*-configuration positions in relation to O atoms from the aqua ligand: (O3) and an O (O1) from pyzdmH2, respectively, which all occupy the equatorial positions. The axial positions are filled by the chlorine from the tetrachloridozincate complex and an O atom from pyzdmH2 (O2) [O(2)–Zn(1)–Cl(1) = 171.37(5)°]. The two pyzdmH2 ligands are in two slightly different conformations regarding the methanol groups. The methanol group O1–H1 attached to the pyrazine ring Cg(1) has the torsion angle ∠O(1)–

$C(1)-C(3)-N(1) = -26.5(3)^\circ$, and the methanol group $O2-H2$, attached to the pyrazine ring $Cg(2)$, has the torsion angle $\angle O(2)-C(2)-C(5)-N(2) = 6.9(3)^\circ$. The tetrahedral coordination geometry of Zn^{2+} is determined by four chloride ions that are coordinated in both bridging and terminal modes [$Zn2-Cl1 = 2.3115(6)$, $Zn2-Cl2 = 2.2773(6)$, $Zn2-Cl3 = 2.2529(6)$, $Zn2-Cl4 = 2.2531(6)$ Å]. Table S2 summarizes the bond lengths, bond, and torsion angles that have been selected for the compound **2**.

The symmetry-related adjacent octahedral zinc centers are bridged by the two pyzdmH2 linkers to create a 1D zig-zag chain along the b crystallography axis (Figure 6c). In compound **2**, strong intra-chain hydrogen bond interactions were identified, including *intra* $O1-H1 \cdots O3 = 2.68(3)$, $O3-H3B \cdots O2 = 2.88(4)$, $C6-H6 \cdots Cl2 = 2.77(4)$, and $C6-H6 \cdots Cl1 = 2.86(4)$ Å. In addition, halogen $\cdots\pi$ (pyrazine ring) and $O-H \cdots ring$ (chelate ring) interactions are observed, including *intra* $Cl4 \cdots Cg(1) = 3.2821(11)$ and *intra* $O3-H3B \cdots Cg(4) = 3.00(4)$ Å. These interactions, likely along with the constraint imposed by the chelation on the $N1-Zn1-O1$ and $N2-Zn1-O2$ angles, contribute to the distortion of the octahedral geometry around $Zn1$. The five-membered chelate rings, $Cg(3) = Zn1-O1-C1-C3-N1$, $Cg(4) = Zn1-O2-C2-C5-N2$, have a bite distance of 2.578 and 2.598 Å and an angle of $\angle O1-Zn1-N1$ and $\angle O2-Zn1-N2$ 75.53(7) and 74.94(7)°, respectively (Figure 7a–c see Tables S8 and S9) [41]. Adjacent one-dimensional zig-zag chains in **2** are connected in a side-by-side manner by the crystal water molecules through three inter-chain hydrogen bonds, resulting in the construction of a 2D sheet that extends within the ab plane. The hydrogen bonds were created between the crystal water molecule and the OH group of pyzdmH2 and the chloride atoms from the tetrachloridozincate complex [$O1-H1 \cdots O4^{iii}$, $O4-H4A \cdots Cl4$, and $O4-H4B \cdots Cl2$] (see Tables 1 and S8). It should be highlighted that a brief $O \cdots O$ distance is present in the hydrogen bond interaction between $O1-H1$ and $O4^{iii}$, with the distance and angle measuring 2.59(3) Å and 174.74°, respectively, for $O1 \cdots O4^{iii}$ and $\angle O1-H1 \cdots O4^{iii}$ [42] (Table S10). The stacking of these sheets along the c direction through the hydrogen bond types of $O-H \cdots Cl$, $C-H \cdots O$, and $C-H \cdots Cl$, with distances between 2.25–3.03 Å, yields a 3D supramolecular structure in which the crystal water molecules have been trapped. The hydrogen bond interactions, as well as the halogen bond interactions which are depicted in Figure 7d and listed in Tables S8 and S10, respectively, contribute to the stacking. Figure 8a,b illustrate the one-dimensional polymeric zig-zag chain structure, as well as the supramolecular structure containing crystal water molecules in **2**.

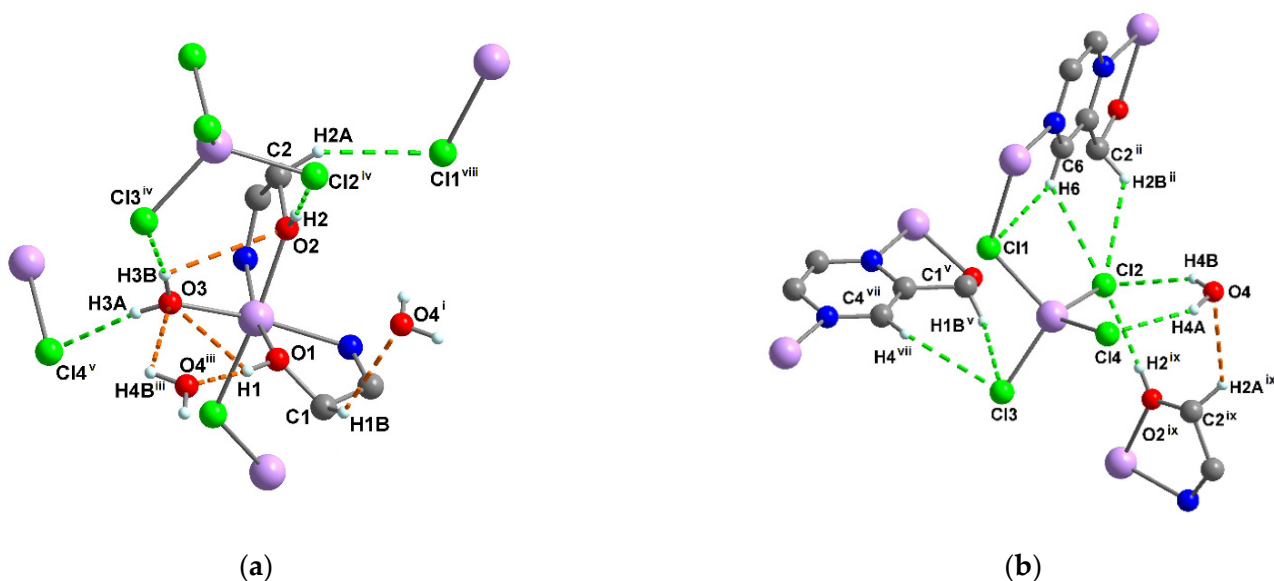


Figure 7. Cont.

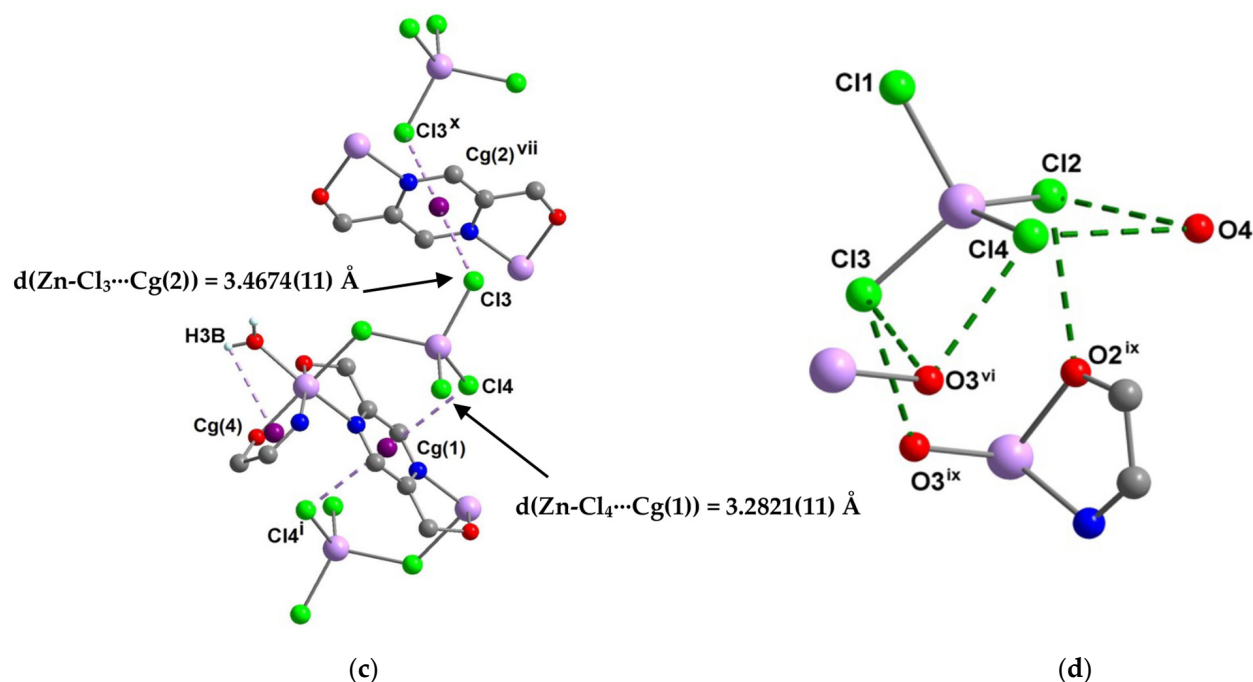


Figure 7. (a,b) Hydrogen bond types O-H...O, O-H...Cl, C-H...O, and C-H...Cl in the structure of **2**, depicted by dashed bonds in orange, light green, orange, and light green, respectively. (c) The halogen bond type Cl... π (pyrazine) and O-H...ring(5-membered chelate ring) interaction is depicted by dashed bonds in light purple. (d) Halogen bond interaction O...Cl is depicted by dashed bonds in dark green. For clarity, only the atoms involved in the short interactions are shown. Symmetry codes: i = 1 - x, 1 - y, 1 - z, ii = 1 - x, 2 - y, 1 - z, iii = x - 1, y, z, iv = x - 1/2, -y + 3/2, z + 1/2, v = -x + 1/2, y + 1/2, -z + 1/2, vi = -x + 1/2, y - 1/2, -z + 1/2, vii = x - 1/2, -y + 3/2, z - 1/2, viii = x + 1/2, -y + 3/2, z + 1/2, ix = x + 1/2, -y + 3/2, z - 1/2, x = -x, 1 - y, -z. Cg(1) = N1-C3-C4#i-N1#i-C3#i-C4, Cg(2) = N2-C5-C6#ii-N2#ii-C5#ii-C6, Cg(3) = Zn1-O1-C1-C3-N1, Cg(4) = Zn1-O2-C2-C5-N2.

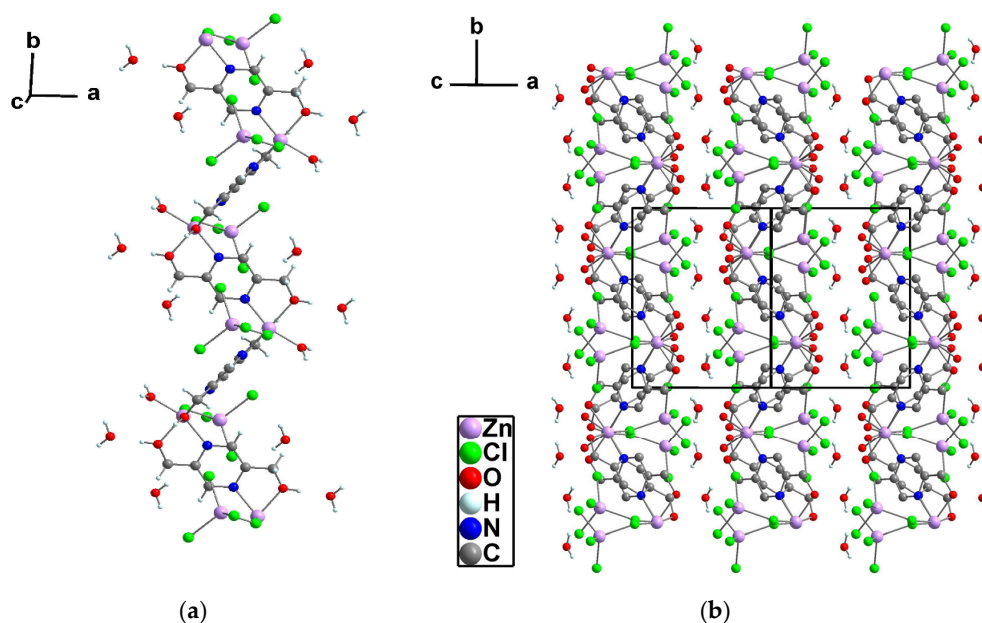


Figure 8. (a) One-dimensional polymeric zig-zag chain structure with crystal water molecules in **2** along the *b* axis. (b) Stacking of the 2D sheets within the *ab* plane in **2**.

3.1.4. Crystal Structure of $[\text{Hg}_2(\text{pyzdmH2})(\mu\text{-Cl})_2(\text{Cl})_2]_n$ (**3**)

In the triclinic system, compound **3** crystallizes in the centrosymmetric space group $P\bar{1}$ (refer to Table S1) as a 1D neutral coordination polymer. The polymeric crystal structure's asymmetric unit contains: two independent mercury Hg^{2+} ions (Hg1 and Hg2), one pyzdmH2 as an organic linker, which forms an unilaterally tridentate chelate linker between the two mercury ions Hg1 and Hg2 with one hanging uncoordinated OH group (O2-H2), two chloride ions acting as bridges that connect the Hg1 and Hg2 ions (Cl1 , Cl2), and two chloride ions, which are terminally coordinated with the Hg2 ion (Cl3 , Cl4). All atoms are in general positions ($Z = 2$, $Z' = 1$). The overall positive charge of the two Hg^{2+} cations was neutralized by the four chloride ions in each formula unit in **3**. In Figure 9, the asymmetric unit of **3** is depicted, which displays two distinct coordination geometries around the Hg^{2+} ions. Specifically, Hg1 exhibits a four-coordinated see-saw-like geometry, while Hg2 displays a five-coordinated square pyramid geometry, as illustrated in Figure 9b,c. The Hg1 cation is chelated by the N, O atoms of pyzdmH2 in the equatorial sites [$\text{Hg1-O1} = 2.642(3)$, $\text{Hg1-N1} = 2.575(3)$ Å]. In addition to this, the Hg1 ion is coordinated by the two independent bridging chloride ions in the axial sites [$\text{Hg1-Cl1} = 2.3491(9)$, $\text{Hg1-Cl2} = 2.3558(8)$ Å], thereby forming a see-saw-like coordination environment around Hg1 . Therefore, the bite distance of the five-membered chelate ring ($\text{Cg}(2) = \text{Hg1-O1-C1-C2-N1}$) is 2.751 Å and gives an angle of $\angle\text{O1-Hg1-N1}$ of $63.63(8)^\circ$ [39]. The Hg2 ion is coordinated by four chloride ions in the equatorial sites, the two terminal chloride ions [$\text{Hg2-Cl3} = 2.3182(9)$, $\text{Hg2-Cl4} = 2.3104(8)$ Å], the bridging chloride ions [$\text{Hg2-Cl1}^i = 3.0705(10)$, $\text{Hg2-Cl2}^i = 3.0502(10)$ Å], and the nitrogen atom from pyzdmH2 in the axial position [$\text{Hg2-N2} = 2.710(3)$ Å], to form a distorted square pyramid geometry. The Hg2 ion lies out of the square plane, which was created by Cl1^i , Cl3 , Cl2^i , and Cl4 with an r.m.s deviation of 0.114 Å. The selected bond lengths, bond, and torsion angles of **3** are summarized in Table S2 (see Table S2 for symmetry codes).

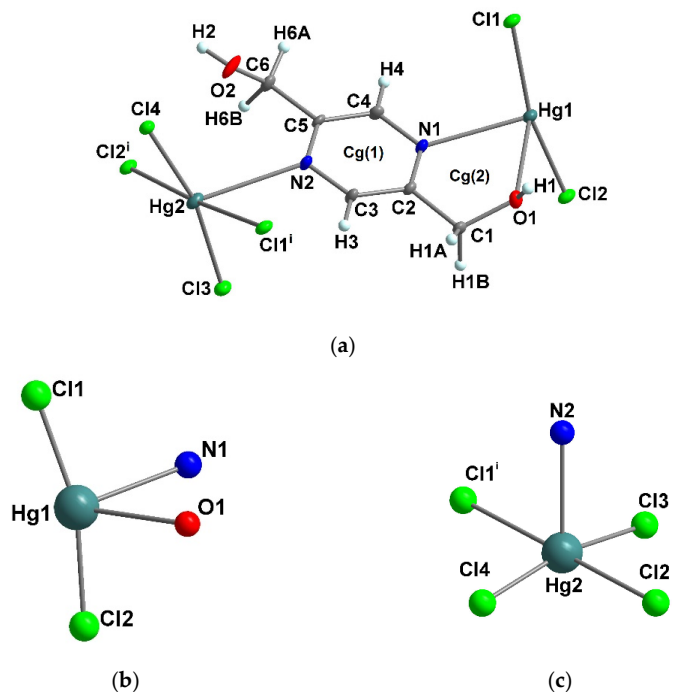


Figure 9. (a) Asymmetric unit for **3**, along with the atom labeling scheme. The atoms defining the asymmetric unit of the crystal structure **3** are indicated without symmetry codes; displacement ellipsoids are at the 50% probability level; H atoms are of arbitrary radii. Symmetry code: $i = 2 - x, 1 - y, 1 - z$. $\text{Cg}(1) = \text{N1-C2-C3-N2-C5-C4}$, $\text{Cg}(2) = \text{Hg1-O1-C1-C2-N1}$. Ball and stick presentations of the coordination environments around (b) Hg1 and (c) Hg2 .

The Hg1 and Hg2 centers are bridged by one pyzdmH2 (Hg1...Hg2 distance of 8.03(4) Å). Additionally, Hg1 and Hg2 are each connected to adjacent Hg2 and Hg1 centers via two pairs of the bridging Cl atoms, with the Cl1-Hg1-Cl2 and Cl1-Hg2-Cl2 angles being 163.73(3)° and 176.69(2)°, respectively. The Hg1...Hg2 distances in these bridging interactions are 3.96(3) Å and 4.01(3) Å. A one-dimensional ladder-like chain was generated through the described connections, which extends along the crystallographic *a*-axis (Figure 10). The hydrogen bonds *intra* O1-H1...O2ⁱ = 1.93(2), O1-H1...Cl4ⁱ = 2.75(2), C3-H3...Cl1ⁱ = 2.81(9), C4-H4...Cl3ⁱⁱ = 2.97(9), and C6-H6B...Cl2ⁱⁱ = 2.95(8) Å, listed from stronger to weaker interaction, were identified in each one-dimensional ladder-like chain (Figure 11a and Table S11). Each polymer chain contains symmetrically arranged aromatic pyrazine rings (Cg(1)) that pack almost parallel (alpha ~0°) and with a small degree of slippage (slippage ~1.5°) as shown in Figure 11b. The distance between the centroids of the pyrazine rings is relatively long and reported in Table S12. The one-dimensional chains are joined together in a side-by-side fashion by hydrogen bonds between the uncoordinated OH group of pyzdmH2 in one chain, the oxygen atom from the coordinated OH group of pyzdmH2, and the chloride atom (Cl2) in a symmetry-related adjacent chain [O2-H2...O1ⁱⁱⁱ = 2.25(3) Å and O2-H2...Cl2ⁱⁱⁱ = 2.82(4) Å] (Table 1). This creates a 2D sheet that extends within the *ac* plane (Figure 11a,d). The stacking of these sheets along the *b* direction through hydrogen bonds of the C-H...Cl type with range distances between 2.95–3.12 Å yields a 3D non-covalent structure (Figure S7, Table S11). Detailed analysis of the crystal structure revealed the *intra*- and *inter* chain Hg...Cl and short halogen bond interactions listed in Tables S11 and S13.

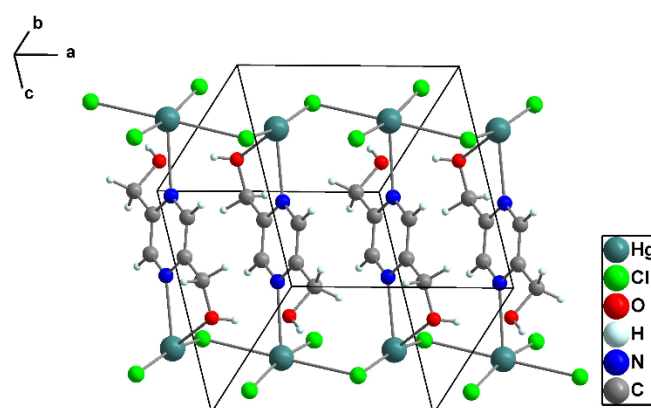


Figure 10. One-dimensional ladder-like chain structure along the *a*-axis in the unit cell.

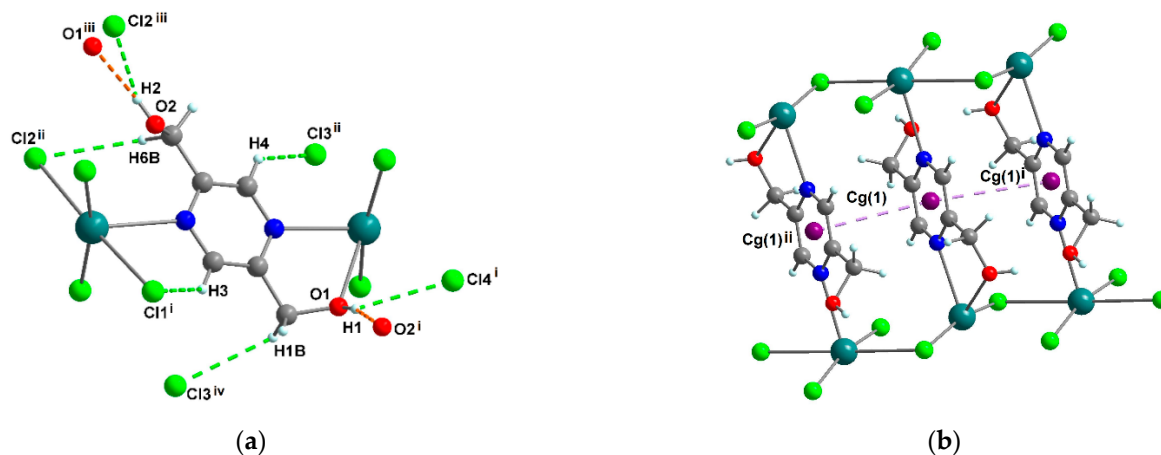


Figure 11. Cont.

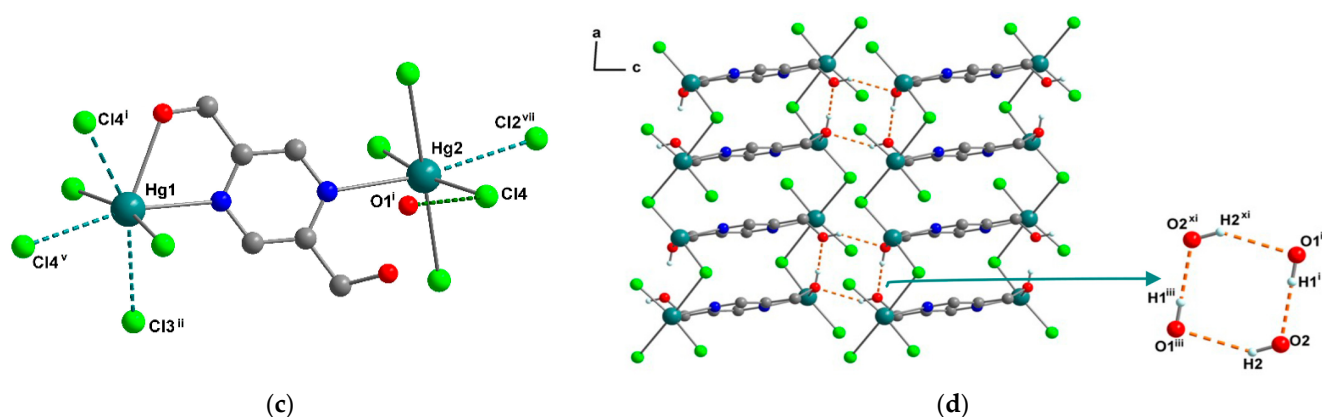


Figure 11. (a) Hydrogen bonds of the O-H...O, O-H...Cl, and C-H...Cl types are depicted by dashed bonds in orange and light green, respectively. (b) π - π (pyrazine ring) interactions are depicted by dashed bonds in light purple. (c) *intra*- and *inter*-chain Hg...Cl and halogen bond O Cl interactions are depicted by blue-green and emerald green, respectively. (d) 2D sheet created by the hydrogen bonds of the O-H...O and O-H...Cl types in the *ac* plane, along with the magnified depiction of the arrangement of hydrogen bonds of the OH...O type between two one-dimensional ladder-like chains (four-membered cooperative O-H...O-H...O-H...O-H ring). For the sake of clarity, the hydrogens involved in the hydrogen bonds are shown. Symmetry codes $i = -x + 2, -y + 1, -z + 1$, $ii = -x + 1, -y + 1, -z + 1$, $iii = x, y, z - 1$, $iv = -x + 1, -y + 2, -z + 1$, $v = x, y - 1, z + 1$, $vii = x, y + 1, z - 1$, $xi = 2 - x, 1 - y, -z$.

3.1.5. Crystal Structure of $\{[\text{Cd}_2(\text{pyzdmH}_2)(\mu\text{-Cl})_4]\cdot\text{H}_2\text{O}\}_n$ (**4**)

Compound **4** crystallizes in the monoclinic centrosymmetric $C2/c$ space group (Table S1). The structure of **4** is a 3D neutral coordination polymer, in which the Cd^{2+} ion has one type of coordination geometry: a distorted octahedral geometry. As displayed in Figure 12a, the asymmetric unit of the polymeric crystal structure contains one cadmium ion (Cd^{2+}) and half of pyzdmH2, which forms a bridging tetra-dentate characteristic linker, two chloride ions, which are coordinated to the cadmium ion in bridging fashion (Cl1 and Cl2), and a non-coordinated crystal water molecule (O2H2AH2B) near a special position ($Z = 4$, $Z' = 0.5$). The positive charge on the Cd^{2+} ion is balanced by the two bridging chloride ions.

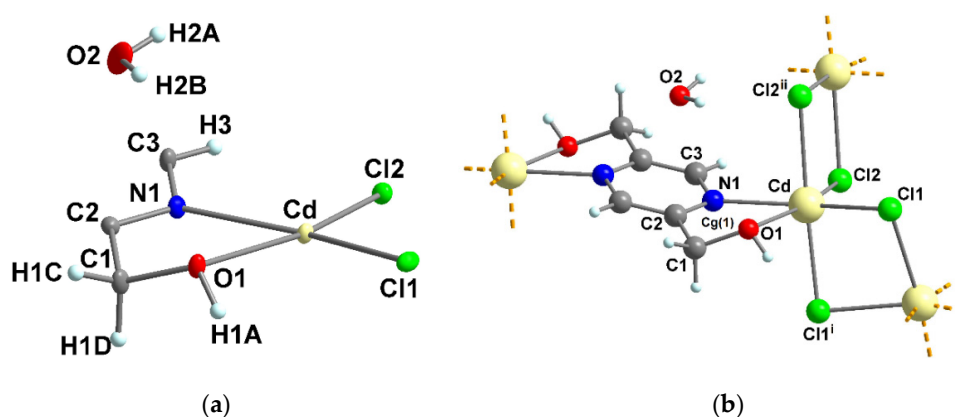


Figure 12. (a) Asymmetric unit of **4** along with the atom labeling scheme. For the sake of clarity, hydrogen bonds are omitted. Displacement ellipsoids are drawn at the 50% probability level and H atoms are of arbitrary radii. (b) Ball and stick presentation of the full coordination environment around the Cd^{2+} in **4**. Symmetry codes: $i = 1 - x, y, 1/2 - z$, $ii = 1 - x, 1 - y, 1 - z$. (Cg(1) = Cd-O1-C1-C2-N1).

As displayed in Figure 12b, the Cd^{2+} ion is in a distorted octahedral coordination geometry by the four bridging chloride ions [$\text{Cd}-\text{Cl1} = 2.5719(11)$, $\text{Cd}-\text{Cl2} = 2.5581(12)$,

$\text{Cd}-\text{Cl1}^{\text{i}} = 2.6055(12)$, $\text{Cd}-\text{Cl2}^{\text{ii}} = 2.6752(12)$ Å] and the oxygen and nitrogen atoms from pyzdmH2 [$\text{Cd}-\text{O1} = 2.416(3)$, $\text{Cd}-\text{N1} = 2.367(4)$ Å]. The chelating N and O atoms from pyzdmH2 (N1 and O1) are *trans* to the chloride ions Cl1 and Cl2, respectively, and the $\angle\text{N1}-\text{Cd}-\text{O1}$ and $\angle\text{Cl2}-\text{Cd}-\text{Cl1}$ bond angles are $69.36(13)$ and $109.07(4)^\circ$, respectively. The $\text{N1}\cdots\text{O1}$ bite distance in the five-membered chelate ring is 2.723 Å [39]. The torsion angle $\angle\text{O1}-\text{C1}-\text{C2}-\text{N1}$ in the chelate ring is $-36.9(5)^\circ$ (Figure 12b). The angle between the *trans*-positioned chloride ions, $\angle\text{Cl1}^{\text{i}}-\text{Cd}-\text{Cl2}^{\text{ii}}$, is $173.47(4)^\circ$. The bridging chloride ions have slightly different bond distances to the Cd ions, with $\text{Cd}-\text{Cl1}$ and $\text{Cd}-\text{Cl2}$ being shorter than $\text{Cd}-\text{Cl1}^{\text{i}}$ and $\text{Cd}-\text{Cl2}^{\text{ii}}$. The shorter $\text{Cd}-\text{Cl1}$ and $\text{Cd}-\text{Cl2}$ distances can be rationalized on the basis of their *trans*-position to the N and O donors and the resulting *trans*-influence: the stronger π -donating chloride ligands are *trans* to the weaker π -donating N and O atoms and can form shorter Cd-Cl bonds than the two *trans*-positioned chloride ligands competing for the same d-orbital for π -donation. Table S2 lists the selected bond lengths, bond, and torsion angles in 4.

Each Cd^{2+} center is connected to three neighboring Cd^{2+} centers through the four bridging chloride ions (Cl1, Cl1ⁱ, Cl2, Cl2ⁱⁱ) and one bridging tetra-dentate organic linker pyzdmH2. The $\text{Cd}\cdots\text{Cd}$ separations through Cl1, Cl2, and pyzdmH2 are 3.69(6), 3.84(5), 7.46(7) Å, respectively. The Cd^{2+} ion connection to the four bridging chloride ions Cl1, Cl1ⁱ, Cl2, and Cl2ⁱⁱ constructs a crenellation-like chain along the crystallographic *c*-axis (Figure 13a). The chain consists of two types of four-membered rings with square planes, where the dihedral angle between adjacent rings is 82.9° and the bond angles $\angle\text{Cd}-\text{Cl1}-\text{Cd}^{\text{i}}$ and $\angle\text{Cd}-\text{Cl2}-\text{Cd}^{\text{ii}}$ are $90.96(4)$ and $94.51(4)^\circ$, respectively (Figure 13b). These two types of four-membered rings alternately repeat along the crystallographic *c*-axis to construct the crenellation-like chain (Figure 13a). It is appropriate to mention that the distortion from the octahedral geometry around Cd^{2+} is due to the angle strain present in the four-membered ring Cg(3) and the constraint imposed by the chelation on the bond angle $\angle\text{N1}-\text{Cd}-\text{O1}$. Each crenellation-like chain connects to the four neighboring crenellation-like chains through the pyzdmH2 linkers so that a 3D coordination network is generated (Figure 13c,d). The 3D network accommodates crystal water molecules with four hydrogen bonds $\text{O2}-\text{H2B}\cdots\text{O1}^{\text{iv}} = 1.85$, $\text{O1}-\text{H1A}\cdots\text{O2}^{\text{x}} = 1.83(10)$, $\text{O2}-\text{H2A}\cdots\text{Cl2}^{\text{ii}} = 2.65(13)$, and $\text{O2}-\text{H2A}\cdots\text{Cl2}^{\text{v}} = 2.68(13)$ Å (Figures 14b and 15a, Tables 1 and S14), through which an infinite hydrogen-bond chain $\text{O}-\text{H}\cdots\text{O}-\text{H}\cdots\text{O}-\text{H}\cdots$ is formed between the two crenellation-like chains in 4 (Figure 15d). Figure S8a depicts the asymmetric unit where H1B is attached to the oxygen atom from pyzdmH2.

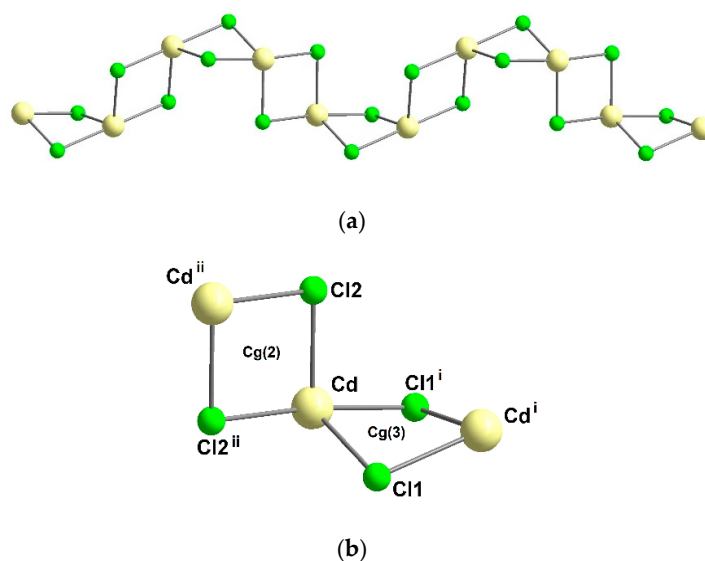


Figure 13. Cont.

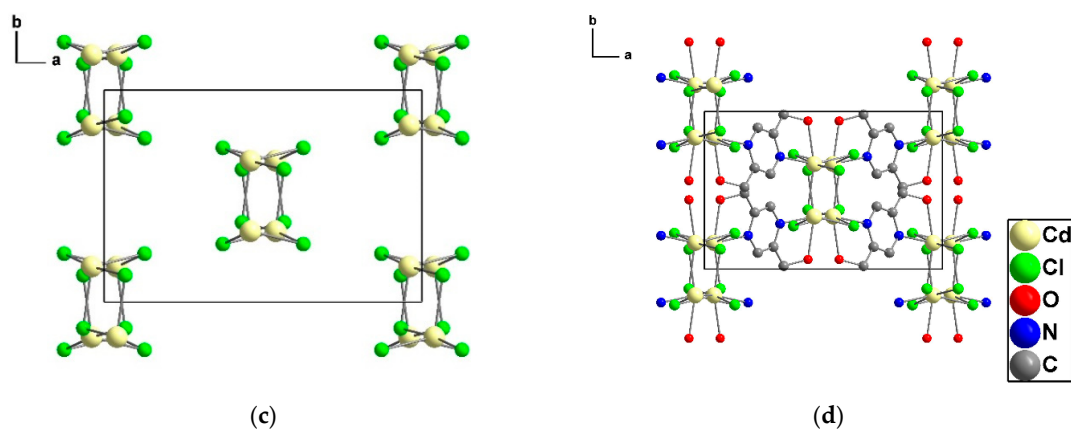


Figure 13. (a) One-dimensional crenellation-like chain structure constructed from Cd and Cl atoms in **4**. (b) Two alternating square-like rings Cg(2) and Cg(3), ((Cg(2) = Cd, Cl2, Cdⁱⁱ, Cl2ⁱⁱ with r.m.s deviation of 0.000 Å and Cg(3) = Cd, Cl1, Cdⁱ, Cl1ⁱ with r.m.s deviation of 0.265 Å). (c) Ball and stick presentation of the five crenellation-like chains. (d) The unit cell of **4** viewed along the *c*-axis. Hydrogen atoms and crystal water molecules omitted for the sake of clarity. Symmetry codes: I = $-x + 1, y, -z + \frac{1}{2}$, ii = $-x + 1, -y + 1, -z + 1$.

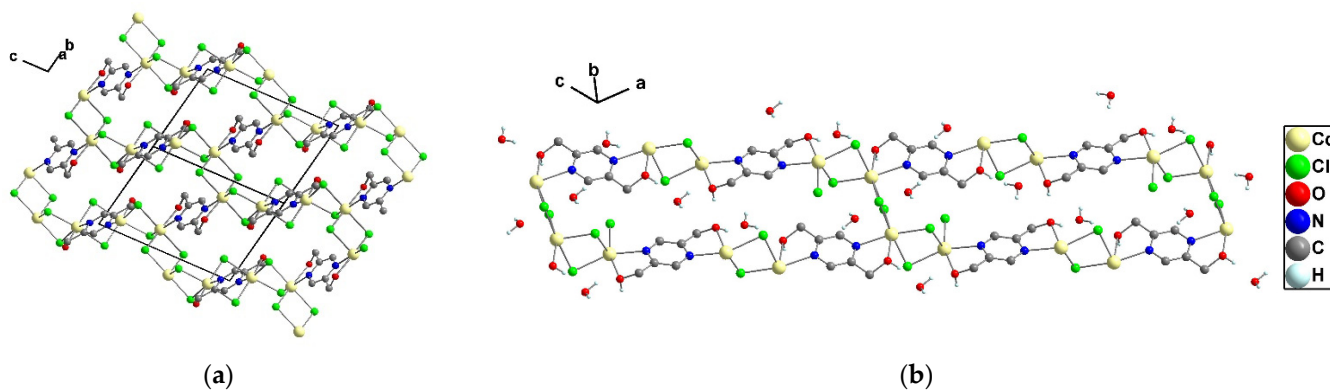


Figure 14. (a) The unit cell packing within the *bc* plane. For the sake of clarity, H atoms and the crystal water molecules are omitted. (b) Simplified view of the empty space along with the crystal water molecules in **4**. For the sake of clarity, H atoms from the crystal water molecules and hydroxyl groups only are depicted.

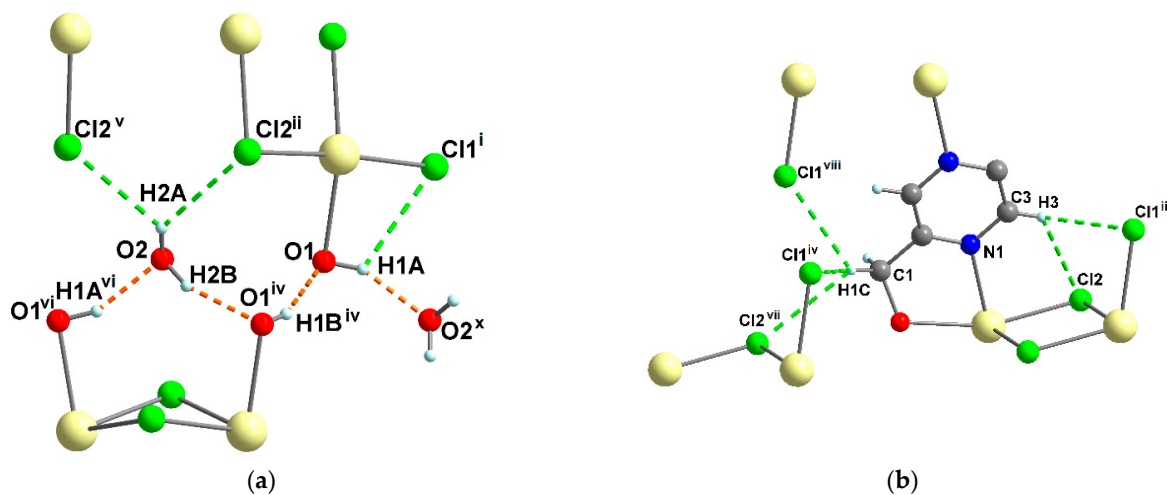


Figure 15. Cont.

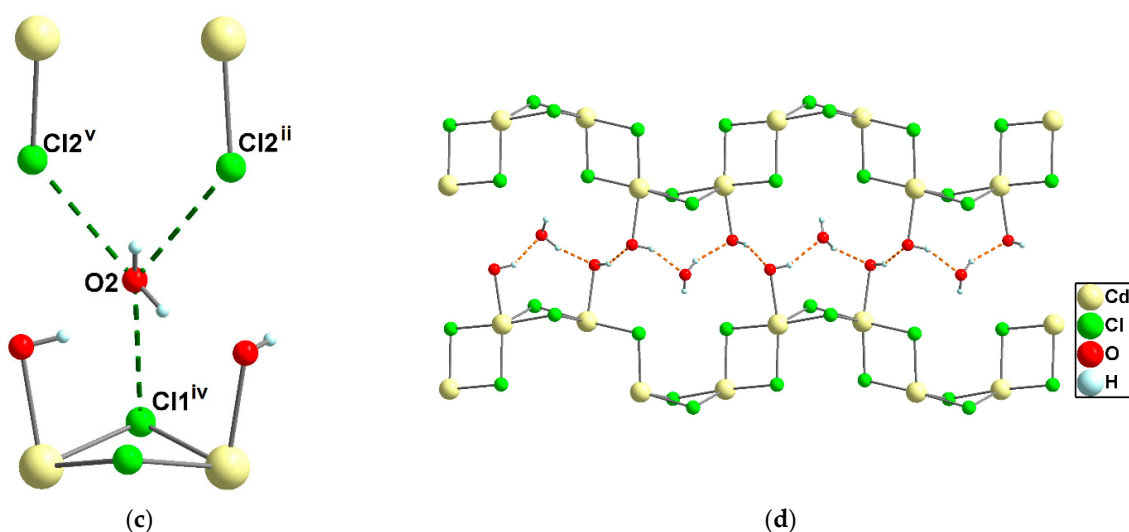


Figure 15. (a) Hydrogen bonds of the O-H...O and O-H...Cl types are depicted by dashed bonds in orange and light green, respectively. (b) Hydrogen bonds of the C-H...Cl type and (c) halogen bond interactions are depicted by dashed bonds in light and dark green, respectively. (d) Zig-zag arrangement of crystal water molecules in **4**. Symmetry codes: i = 1 − x, y, 1/2 − z, ii = −x + 1, −y + 1, −z + 1, iii = −x + 1/2, −y + 1/2, −z + 1, iv = −x + 1, −y, −z + 1, v = x, 1 − y, 1/2 + z, vi = x, −y, 1/2 + z, vii = x, −1 + y, z, viii = x − 1/2, y − 1/2, z, x = x, −y, −1/2 + z.

Upon conducting a comprehensive analysis of the crystal structure through the PLATON full geometry calculation, multiple hydrogen bond and halogen bond interactions were identified and are presented in Figure 15 and listed in Tables S14 and S15. Table 1 lists the strongest hydrogen bond interactions found in the crystal structure [41–46].

3.1.6. Crystal Structure of $\{[\text{Cd}_2(\text{pyzdmH}_2)(\mu\text{-Br})_4]\cdot\text{H}_2\text{O}\}_n$ (**5**)

The results of single-crystal X-ray diffraction analysis revealed that compound **5** has an isostructural relationship to compound **4**. Both compounds share the same space group (monoclinic centrosymmetric $C2/c$) and have similar atomic arrangements, but their chemical compositions differ due to the replacement of Cl in compound **4** with Br in compound **5**. Although the crystallographic parameters of the two structures are not identical, they exhibit a high degree of similarity (Table S1). The unit cell parameters of **5** are within 3.6% of those of **4**, with the lattice constants *a*, *b*, and *c* being 14.12, 9.00 Å, and 12.02 Å, respectively, compared to 14.02, 8.69, and 11.70 Å in **4**. The value of the beta angle in **5** is 109.6(3)° compared to 111.1(2)° in **4**. The asymmetric unit in **5** contains: one independent cadmium ion (Cd^{2+}) with a distorted octahedral coordination geometry, half of pyzdmH₂, which forms a bridging tetra-dentate characteristic linker, two bromine ions, which are coordinated with the cadmium ion in a bridging fashion (Br1 and Br2), and finally a non-coordinated water molecule (O2H₂AH₂B) near a special position ($Z = 4$, $Z' = 0.5$). All atoms are in general positions. Figure 16a,b show the asymmetric unit and the full coordination environment around the Cd ion.

The structure of **5** has a similar coordination geometry around the Cd^{2+} ion as the chloride compound **4**. The Cd^{2+} ion is coordinated by the four bridging bromine ions and the nitrogen and oxygen atoms from pyzdmH₂ so that the bite distance in the five-membered chelate ring ($\text{Cg}(1) = \text{Cd}-\text{O1}-\text{C1}-\text{C2}-\text{N1}$) is 2.74 Å. The equatorial plane is occupied by the chelating N and O atoms from pyzdmH₂ and the two bridging bromides (Br1, Br2), and the axial positions are occupied by the two symmetry-related bridging bromides (Br1ⁱ, Br2ⁱⁱ). The selected bond lengths, angles, and torsion angles for **4** and **5** can be compared in Table S2. (See Table S1 for symmetry codes).

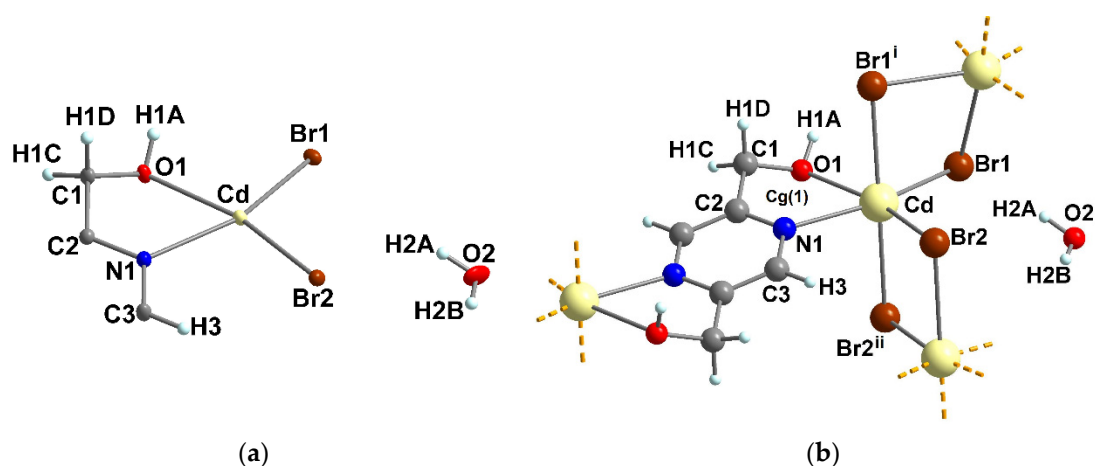


Figure 16. (a) Asymmetric unit of the crystal structure 5 along with the atom labeling scheme. For the sake of clarity, hydrogen bonds are omitted. Displacement ellipsoids are drawn at a 50% probability level and H atoms are of arbitrary radii. (b) Ball and stick presentation of the full coordination environment around Cd^{2+} in 5. Symmetry codes: $i = 1 - x, y, -z + 3/2$ and $ii = 1 - x, 1 - y, 1 - z$.

The 3D structure of 5 is analogous to 4, where Cd^{2+} centers are linked to neighboring Cd^{2+} centers via the bridging bromide ions (Br1 , Br1^i , Br2 , Br2^{ii}), resulting in a crenellation-like chain structure along the crystallographic c -axis (Figure S8a,b) and the bridging tetra-dentate organic linker pyzdmH2 (Figure S8c,d). In the 3D structure, the $\text{Cd}\cdots\text{Cd}$ distances which are separated by the bridging bromide ions and pyzdmH2, are $3.7981(6)$ Å, $3.9635(5)$ Å, and $7.4928(7)$ Å, respectively. As depicted in Figure 17a, the water molecules in the 3D coordination network are accommodated by the hydrogen bond interactions involving $\text{O1-H1A}^v\cdots\text{O2}$, $\text{O2-H2B}\cdots\text{O1}^v$, $\text{O2-H2B}\cdots\text{Br2}$, and $\text{O2-H2B}\cdots\text{Br2}^i$ (Figure S9a,b) [47]. Like structure 4, structure 5 also has infinite chains of $\text{O-H}\cdots\text{O-H}\cdots\text{O-H}\cdots$, which result from the hydrogen bond interactions between the hydroxyl groups of pyzdmH2 and crystal water molecules in 5. The hydrogen bond distances are listed in Table 1. Figure 17b shows the arrangement of the crystal water molecules between two crenellation-like chains in 5. Several non-covalent interactions involving hydrogen bonds and halogen bonds have been identified in 5 and listed in Tables S16 and S17.

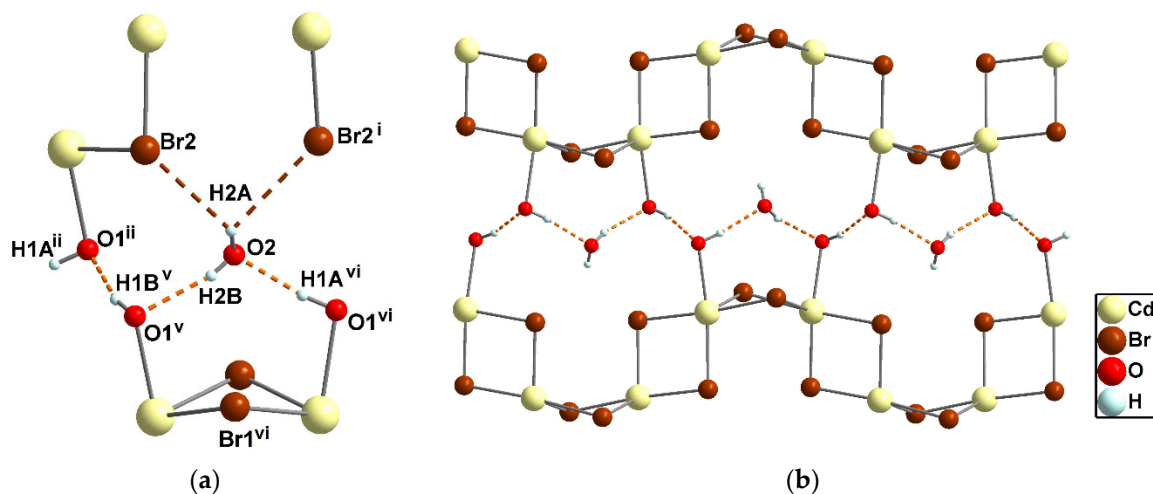


Figure 17. (a) Hydrogen bonds of the $\text{O-H}\cdots\text{O}$ and $\text{O-H}\cdots\text{Br}$ types are depicted by dashed bonds in orange and brick red, respectively. (b) Zig-zag arrangement of crystal water molecules in 5. Symmetry codes: $i = -x + 1, y, -z + 3/2$, $ii = -x + 1, -y + 1, -z + 1$, $v = x, y + 1, z$, $vi = 1 - x, y + 1, 3/2 - z$.

3.2. IR Studies

Based on the comparison of the IR spectra of pyzdmH2, **2**, **3**, and **5**, certain vibrations were identified (Figures S10–S13). These vibrations correspond to O-H_{alcohol} and O-H_{crystal water} which are involved in strong hydrogen bond interactions. In **2**, the vibrations of O-H_{alcohol} and O-H_{crystal water} were identified as 3408, 3340, 3269, and 3183 cm^{−1}. In **3**, the vibrations of O-H_{alcohol} were assigned to 3486 and 3275 cm^{−1}, and in the absence of crystal water there were no vibrations of O-H_{crystal water}. In **5**, the vibrations of O-H_{alcohol} were found at 3546 and 3419 cm^{−1}, while the vibrations of O-H_{crystal water} were identified as 3108 and 1587 cm^{−1}. The vibrations of C-H_{aromatic} and C-H_{aliphatic}, involved in the formation of the hydrogen bonds, were identified as 3033, 2827, and 2808 cm^{−1} (Figures S10–S13) [48]. The IR and CHN analyses confirmed the presence of crystal water molecules in **2** and **5**, as well as the strong hydrogen bond interactions observed in the single crystal structures of **2**, **3**, and **5**.

4. Conclusions

In this paper, we reported the synthesis and crystal structures of pyrazine diylidimethanol (pyzdmH2) and three 1D (**1–3**) and two isostructural 3D coordination compounds (**4**, **5**). The structures of **1–5** were assembled from pyzdmH2 with the metal halide salts of CuBr₂, ZnCl₂, HgCl₂, CdCl₂·H₂O, and CdBr₂·4H₂O in water under ambient conditions, respectively. With the exception of compound **3**, **1–5** each contained crystal water molecules within their structures. PyzdmH2, which acts as a bridging tetra-dentate linker with N,O-chelating capability in the reported structures **1–5** (tri-dentate in **3**), is weakly acidic. The OH groups in the methanol parts were not intended to be de-protonated and have provided a possibility of forming strong hydrogen bond interactions. The 1D and 3D coordination compounds featured strong hydrogen bonds between the hydroxyl groups from the organic ligand, coordinated, and non-coordinated water molecules in the structures. This includes the OH···O type hydrogen bond interaction, in which the hydroxyl group as a donor and oxygen atom as an acceptor with the bond distance ranges from 1.72–2.87 Å, the OH···X (X = N, Cl, Br) type hydrogen bond interaction, in which the hydroxyl group as a donor and nitrogen or halogen atoms as an acceptor with the bond distance ranges from 1.97–3.21 Å, and the C-H_{aromatic}/C-H_{aliphatic}···X (X = O, Cl, Br) type hydrogen bond interactions, in which the C-H_{aromatic} and C-H_{aliphatic} groups as donors and the oxygen or halogen atom as an acceptor with the bond distance ranges from 2.42–3.24 Å. The short halogen bond interaction of the donor halogens (Br, Cl) with the electronegative heteroatom (O), with the bond distance ranging from 3.08–3.48 Å, has been found in **1–5**. The results showed that both bridged pyzdmH2 and halogen ions, as well as the hydrogen bond interactions involved with the hydroxyl groups from pyzdmH2, and water molecules play the most important roles in the 3D non-covalent and covalent structure construction in **1–5**. Given the high water solubility and versatility of pyzdmH2 as a bridging tetra-dentate organic linker with N,O-chelating ability, capable of engaging in various non-covalent interactions as seen in the newly synthesized compounds, we are motivated to synthesize and investigate other ligand derivatives with elongated or angled skeletons for fabricating porous coordination compounds. Such compounds can be synthesized without using hazardous organic solvents, elevated temperature, or pressure, and have potential applications in reversible adsorption of small molecules or biologically relevant molecules, owing to the presence of hydroxyl groups, hydrophilic pores, voids, or empty spaces, and have the ability to form robust hydrogen bonding networks. This presents an exciting research direction that has been long sought after.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13081193/s1>, **Section S1.** NMR spectra of dimethyl pyrazine-2,5-dicarboxylate and pyrazine-2,5-diylldimethanol (pyzdmH2); **Section S2.** Listings of crystallographic data, structure determination and refinement details for pyzdmH2, and 1–5; **Section S3.** Infrared spectra of compounds 2, 3 and 5; **Section S4.** Powder X-ray diffractograms of compounds 2, 3 and 5. CCDC numbers 2232274, 2232622, 2253333, 2236315, 2249852, and 2236379 for pyzdmH2 and 1–5, respectively. The ^1H and ^{13}C NMR spectra for dimethyl pyrazine-2,5-dicarboxylate and pyzdmH2. Crystallographic data including structure determination and refinement details as well as selected bond lengths, angles, and torsion angles for pyzdmH2 and 1–5. Tables listing the data for short non-covalent interactions for pyzdmH2 and 1–5. Reciprocal lattice plot of the non-merohedral twin crystal 2. Crystal packing diagram of pyzdmH2, 3 and 5. IR spectra of 2, 3, and 5.

Author Contributions: Conceptualization, M.A.; methodology, M.A.; software, M.A.; validation, C.J. and T.S.; formal analysis, M.A.; investigation, M.A.; resources, C.J.; data curation, M.A.; writing—original draft preparation, M.A.; writing—review and editing, M.A. and C.J.; visualization, M.A.; supervision, C.J. and M.A.; project administration, M.A.; funding acquisition, C.J. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The datasets generated and analyzed during the current study are available at Heinrich Heine University. For inquiries or collaboration opportunities, please contact Dr. Mahsa Armaghan.

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Conflicts of Interest: The authors declare no conflict of interest.

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