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# Multidimensional Metal–Organic Frameworks Constructed from Flexible Bis(imidazole) Ligands

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**ABSTRACT:** Two structurally related flexible bis(imidazole) ligands, *N,N'*-(1,1-methyl)bis(imidazole) (**L**<sup>1</sup>) and *N,N'*-(1,4-butanediyl)bis(imidazole) (**L**<sup>2</sup>) reacted with Ag<sup>I</sup>, Cu<sup>II</sup>, Zn<sup>II</sup>, and Cd<sup>II</sup> salts under hydrothermal conditions (except for **2** at room temperature), resulted in the formation of eight novel metal–organic coordination architectures, from one-dimensional (1D) chain to three-dimensional (3D) network structures: {[Ag(**L**<sup>1</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>n</sub>} (**1**), {[Cu(**L**<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](Cl<sub>2</sub>(H<sub>2</sub>O)<sub>0.5</sub>(acetone))<sub>n</sub>} (**2**), {[Cu(**L**<sup>1</sup>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>)<sub>n</sub>} (**3**), {[Cu(**L**<sup>1</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>)<sub>n</sub>} (**4**), {[Zn(**L**<sup>1</sup>)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>)<sub>n</sub>} (**5**), {[Cd(**L**<sup>1</sup>)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>)<sub>n</sub>} (**6**), {[Cd(**L**<sup>1</sup>)<sub>2</sub>](N<sub>3</sub>)<sub>2</sub>)<sub>n</sub>} (**7**), and {[Zn(**L**<sup>2</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>)<sub>n</sub>} (**8**). All complexes have been structurally characterized by X-ray diffraction analysis. In **1**, the Ag<sup>I</sup> centers are two-coordinate with linear geometry and **L**<sup>1</sup> ligands bridge the Ag<sup>I</sup> centers to form 1D single helical chains. **2** and **7** have 1D double chain structures with the central metal ions being six-coordinated by four discrete **L**<sup>1</sup> and two apical ligands (water molecules for **2** and N<sub>3</sub><sup>−</sup> for **7**). **3** and **4** are isostructural two-dimensional (2D) (4,4) networks with square planar Cu<sup>II</sup> centers. **5** and **6** also are isostructural with CdSO<sub>4</sub>-like 3D framework structures. In **8**, the Zn<sup>II</sup> ions are tetrahedral, and each **L**<sup>2</sup> ligand links two Zn<sup>II</sup> ions to form a 1D double chain.

## Introduction

Metal coordination polymers with multidimensional-ity have attracted great current interest in coordination chemistry because of their intriguing structures and potential as functional materials.<sup>1</sup> Studies in this field have been focused on the design and construction of novel coordination frameworks and the relationships between their structures and properties. It is still a great challenge to predict the exact structures and composition of the assembly products built by coordination bonds and/or hydrogen bonds in crystal engineering.<sup>2</sup> Several factors, such as the coordination nature of the metal ions, ligand structure, counteranions, and so on, which may be the key for the rational design of crystalline materials, highly influence the formation of such frameworks. Therefore, systematic research on this topic is still important for understanding the roles of these factors in the formation of metal coordination frameworks.

In recent years, there is an increasing interest in coordination architectures built by flexible bridging ligands.<sup>3</sup> Coordination architectures with diverse structures of different types of flexible bridging ligands have been reported, particularly those containing S-, N-, or O-donors. The bis(imidazole) ligands bearing alkyl spacers are a good choice of a N-donor ligand, and the flexible nature of spacers allows the ligands to bend and rotate when coordinating to metal centers so as to

conform to the coordination geometries of metal ions. Significant progress has been achieved by Goodgame and others in this area;<sup>4</sup> however, the factors that affect the formation of coordination frameworks constructed from flexible bis(imidazole) ligands and the exploitation of new synthetic methods are still comparatively less investigated.

In our continuing interest in studies on the influence of metal ions, counteranions, and ligand spacers on the framework structures, in this paper, two flexible ligands *N,N'*-(1,1-methyl)bis(imidazole) (**L**<sup>1</sup>) and *N,N'*-(1,4-butanediyl)bis(imidazole) (**L**<sup>2</sup>) (Chart 1) were reacted with several metal salts and eight new complexes, {[Ag(**L**<sup>1</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>n</sub>} (**1**), {[Cu(**L**<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](Cl<sub>2</sub>(H<sub>2</sub>O)<sub>0.5</sub>(acetone))<sub>n</sub>} (**2**), {[Cu(**L**<sup>1</sup>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub>)<sub>n</sub>} (**3**), {[Cu(**L**<sup>1</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>)<sub>n</sub>} (**4**), {[Zn(**L**<sup>1</sup>)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>)<sub>n</sub>} (**5**), {[Cd(**L**<sup>1</sup>)<sub>3</sub>](ClO<sub>4</sub>)<sub>2</sub>)<sub>n</sub>} (**6**), {[Cd(**L**<sup>1</sup>)<sub>2</sub>](N<sub>3</sub>)<sub>2</sub>)<sub>n</sub>} (**7**), and {[Zn(**L**<sup>2</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>)<sub>n</sub>} (**8**), were obtained. Herein, we report the synthesis and structures of these complexes.

## Experimental Section

**Materials and General Methods.** Solvents and starting materials for synthesis were purchased commercially and used as received. The ligands **L**<sup>1</sup> and **L**<sup>2</sup> were prepared according to reported procedures.<sup>5</sup> Elemental analyses were carried out on a Perkin-Elmer 240C analyzer. IR spectra (KBr pellets) were taken on a FT-IR TENSOR 27 (BRUKER) spectrometer. Thermal stability (TG-DAT) studies were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800 °C. The counteranion exchange experiments were carried out according to reported procedures.<sup>6</sup>

**Synthesis of Complexes.** The single crystals of complexes **1**, and **3–8** were obtained by a hydrothermal method as follows: a mixture of metal salt (1 mmol, AgClO<sub>4</sub>, Cu(BF<sub>4</sub>)<sub>2</sub>·

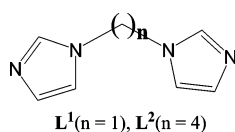
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Chart 1



$6H_2O$ ,  $Cu(ClO_4)_2 \cdot 6H_2O$ ,  $Zn(ClO_4)_2 \cdot 6H_2O$ ,  $Cd(ClO_4)_2 \cdot 6H_2O$ ,  $Cd(NO_3)_2 \cdot 4H_2O$ , or  $Zn(ClO_4)_2 \cdot 6H_2O$  for **1**, **3**, **4**, **5**, **6**, **7**, and **8**, respectively), ligand (for **1**, **3**–**7**,  $L^1$ , 296 mg, 2 mmol; for **8**,  $L^2$ , 380 mg, 2 mmol) and sodium azide (only for complex **7**, 130 mg, 2 mmol) in 10 mL of  $H_2O/C_2H_5OH$  (volume ratio = 4:1) was placed in a Teflon-lined stainless vessel and heated to 140 °C for 48 h. Then the reaction system was cooled to room temperature during 24 h to give rise to the corresponding crystals, which were collected and washed with water.

**1.** Yield: 36%. Anal. Calcd for  $C_7H_8AgClN_4O_4$ : C, 23.65; H, 2.27; N, 15.76. Found: C, 23.47; H, 2.19; N, 15.38. IR (KBr pellet,  $cm^{-1}$ ): 3123m, 3021w, 1709w, 1627w, 1528m, 1401m, 1348w, 1292m, 1241m, 1120s, 1105s, 1081s, 1030m, 947m, 850m, 753w, 712w, 652m, 618s, 453w. DTA data (peak position): 348 °C.

**3.** Yield: 35%. Anal. Calcd for  $C_{14}H_{16}CuB_2F_8N_8$ : C, 31.52; H 3.02; N, 21.00. Found: C, 30.67; H, 2.94; N, 20.38. IR (KBr pellet,  $cm^{-1}$ ): 3161m, 3042w, 1627w, 1538w, 1516m, 1386m, 1358w, 1286m, 1096s, 1001m, 948m, 855m, 765w, 751w, 737m, 710w, 666w, 653w, 614w, 522w, 450w. DTA data (peak position): 344, 388, 467 °C.

**4.** Yield: 16%. Anal. Calcd for  $C_{14}H_{16}CuCl_2N_8O_8$ : C, 30.09; H 2.89; N, 20.05. Found: C, 29.87; H, 2.86; N, 19.91. IR (KBr pellet,  $cm^{-1}$ ): 3140w, 3034w, 1536m, 1514m, 1384w, 1295w, 1239m, 1122s, 1091s, 1061s, 932w, 849wm, 764m, 734mw, 710w, 666w, 653w, 624s, 456w. DTA data (peak position): 311 °C.

**5.** Yield: 27%. Anal. Calcd for  $C_{21}H_{24}ZnCl_2N_{12}O_8$ : C, 35.59; H, 3.41; N, 23.71. Found: C, 35.40; H, 3.32; N, 23.54. IR (KBr pellet,  $cm^{-1}$ ): 3138m, 3032w, 1628m, 1511m, 1402s, 1297m, 1238s, 1116s, 1092s, 951w, 848w, 749w, 725m, 713m, 658, 624s, 561w, 444w. DTA data (peak position): 381 °C.

**6.** Yield: 29%. Anal. Calcd for:  $C_{21}H_{24}CdCl_2N_{12}O_8$ : C, 33.37; H, 3.20; N, 22.24. Found: C, 32.88; H, 3.16; N, 21.88. IR (KBr pellet,  $cm^{-1}$ ): 3128m, 3029w, 1700w, 1592w, 1526m, 1508m, 1401m, 1355w, 1209m, 1233s, 1113s, 1088s, 930m, 844w, 745w, 723w, 715m, 656m, 624s, 448w. DTA data (peak position): 361 °C.

**7.** Yield: 38%. Anal. Calcd for  $C_{14}H_{16}CdN_{14}$ : C, 34.12; H, 3.27 N, 39.79. Found: C, 33.87; H, 3.19; N, 39.08. IR (KBr pellet,  $cm^{-1}$ ): 3112s, 3011m, 2376w, 2036s, 1563w, 1501m, 1422w, 1387w, 1355w, 1284m, 1224s, 1186, 1092s, 1022w, 931m, 838m, 777w, 710w, 659m, 615w. DTA data (peak position): 299, 324 °C.

**8.** Yield: 29%. Anal. Calcd for  $C_{20}H_{28}ZnCl_2N_8O_8$ : C, 37.26; H, 4.38; N, 17.38. Found: C, 37.02; H, 4.29; N, 17.18. IR (KBr pellet,  $cm^{-1}$ ): 3135m, 3053w, 2994w, 2922w, 2826w, 2012w, 1709w, 1619m, 1536s, 1525s, 1446s, 1408w, 1293m, 1246s, 1115s, 980w, 956s, 928m, 841m, 793m, 767m, 659m, 624s, 432w. DTA data (peak position): 353, 414 °C.

**2.** A mixture of  $CuCl_2$  (134 mg, 1 mmol) and  $L^1$  (296 mg, 2 mmol) in water (10 mL) was stirred in room temperature for 20 min, and the resulting solution was refluxed for 3 h to obtain blue precipitate, which was filtered and washed with distilled water. The precipitate was dissolved in a mixed solvent of 5 mL of acetone and 10 mL of DMF and filtered. Blue single crystals were obtained by slow evaporation of the solvent at room temperature for about 20 days (28% yield). Anal. Calcd. for  $C_{17}H_{27}CuCl_2N_8O_{3.5}$ : C, 38.24; H, 5.10; N, 20.99. Found: C, 37.81; H, 4.87; N, 21.32%. IR (KBr pellet,  $cm^{-1}$ ): 3433s, 3036w, 3102w, 3011w, 2371w, 1737w, 1658s, 1534m, 1508m, 1391m, 1359m, 1292m, 1232m, 1096s, 949m, 859m, 765m, 657w, 707w, 561w, 465w. DTA data (peak position): 88, 192, 306 °C.

**Caution!** Although we experienced no problems with the compounds reported in this work, perchlorate salts and azide

salts of metal complexes with organic ligands are potentially explosive and should be handled with great caution.

**X-ray Crystallography.** Intensity data were collected on a Bruker Smart 1000 CCD diffractometer for **1**–**8** with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293 K. The structures were solved by direct methods and refined anisotropically by the full-matrix least-squares technique using the SHELXTL 97 program package.<sup>7</sup> All the non-H atoms were refined anisotropically, while H atoms except for those of water in **2** (which are not located) were included in the calculated positions and refined with isotropic thermal parameters riding on the parent atoms. It should be noted that in the structure of **2** acetone molecules are disordered and locate in the crystallographic  $C_2$  axis and refined by constraint. A summary of the crystallographic data and structure refinements is listed in Table 1. Selected bond lengths and angles for **1**–**8** are listed in Table 2.

## Results and Discussion

**Syntheses and General Characterization.** The crystals of complexes of **1** and **3**–**8** were obtained under hydrothermal conditions. This is different from those of the recently reported flexible bis(imidazole) complexes,<sup>4</sup> which were obtained at room temperature. All the complexes are stable at room temperature and not soluble in water and common organic solvents. The elemental analysis results match well with the composition of crystal structure determination except that of **2**, which may be attributed to the loss of intercalated solvent molecules.

**Thermal Properties of the Complexes.** The TGA studies showed that complexes **1** and **3**–**8** are stable under 200 °C, and decomposition begins at 290, 285, 270, 310, 300, 240 and 305 °C, respectively. For complex **2**, the first weight loss of 13.1% (calc. 12.5%) corresponds approximately to the loss of solvate acetone and lattice water molecules in the temperature range of 45–110 °C, the second weight loss 6.1% (calc. 6.7%) corresponds to the coordinated water molecules in the temperature range of 150–205 °C, and the complex decomposes beyond 260 °C.

**Anion Exchange.** The counteranion exchange could be monitored by the characteristic IR bands of the counteranions.<sup>6</sup> The ion exchange of complex **2** with  $X^-$  ( $X^- = NO_3^-$ ,  $BF_4^-$ ,  $ClO_4^-$ , respectively) was checked after stirring the sample for 20 h in aqueous media at room temperature; the infrared spectra showed the appearance of a strong new  $NO_3^-$  band (1385  $cm^{-1}$ ),  $BF_4^-$  band (1058  $cm^{-1}$ ),  $ClO_4^-$  band (1086  $cm^{-1}$ ), with the rest of the spectrum remaining virtually unchanged. The reversible exchanges were not found. The counteranion exchange of **3** with  $ClO_4^-$  also occurred in aqueous media at room temperature, and the reversible exchanges were not achieved. In addition, the counteranions of complexes **1** and **4**–**8** could not be exchanged.

**Crystal Structures.** **1.** The structure of **1** consists of one-dimensional (1D) cationic polymeric  $\{[Ag(L^1)_2]^+\}_n$  chains and uncoordinated  $ClO_4^-$  anions. The center  $Ag^I$  ion is linearly coordinated by two imidazole nitrogen atoms from different  $L^1$  ligands with an N–Ag–N bond angle of 180° and Ag–N distance of 2.093(3) Å (see Table 2). Each  $L^1$  bridges two  $Ag^I$  ions to form a 1D single helical chain (Figure 1a) in which the adjacent  $Ag \cdots Ag$  distance is 7.778 Å and the dihedral angle of the two imidazole rings in the  $L^1$  ligand is 88.1°. Furthermore, these 1D chains are assembled together

Table 1. Crystallographic Data and Structure Refinement Summary for Complexes 1–8

	1	2	3	4
formula	C <sub>7</sub> H <sub>8</sub> AgClN <sub>4</sub> O <sub>4</sub>	C <sub>17</sub> H <sub>27</sub> CuCl <sub>2</sub> N <sub>8</sub> O <sub>3.5</sub>	C <sub>14</sub> H <sub>16</sub> CuB <sub>2</sub> F <sub>8</sub> N <sub>8</sub>	C <sub>14</sub> H <sub>16</sub> CuCl <sub>2</sub> N <sub>8</sub> O <sub>8</sub>
formula weight	355.49	533.91	533.51	558.79
crystal system	orthorhombic	tetragonal	monoclinic	monoclinic
space group	<i>Pcca</i>	<i>P4(2)/ncm</i>	<i>P2(1)/n</i>	<i>P2(1)/n</i>
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)
<i>a</i> /Å	14.268(4)	12.1263(16)	9.000(2)	9.131(3)
<i>b</i> /Å	5.0065(12)	12.1263(16)	9.140(2)	9.253(3)
<i>c</i> /Å	15.557(4)	17.632(5)	12.421(2)	12.435(4)
$\beta$ /deg	90.00	90.00	91.048(3)	92.580(5)
<i>V</i> /Å <sup>3</sup>	1111.2(5)	2592.8(8)	1021.6(3)	1049.6(5)
<i>Z</i>	4	4	2	2
<i>D</i> /g cm <sup>−3</sup>	2.125	1.368	1.734	1.768
$\mu$ /mm <sup>−1</sup>	2.063	1.083	1.162	1.357
<i>F</i> (000)	696	1104	534	566
reflns measured	5921	14072	5815	5985
obsd reflns	1217	1424	2095	2263
<i>R</i> <sup>a</sup> / <i>wR</i> <sup>b</sup>	0.0357/0.0866	0.0597/0.1727	0.0436/0.1261	0.0470/0.1244
	5	6	7	8
formula	C <sub>21</sub> H <sub>24</sub> ZnCl <sub>2</sub> N <sub>12</sub> O <sub>8</sub>	C <sub>21</sub> H <sub>24</sub> CdCl <sub>2</sub> N <sub>12</sub> O <sub>8</sub>	C <sub>14</sub> H <sub>16</sub> CdN <sub>14</sub>	C <sub>20</sub> H <sub>28</sub> ZnCl <sub>2</sub> N <sub>8</sub> O <sub>8</sub>
formula weight	708.79	755.82	492.81	644.77
crystal system	monoclinic	monoclinic	monoclinic	tetragonal
space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/m</i>	<i>I4(1)/acd</i>
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)
<i>a</i> /Å	12.348(5)	12.632(5)	16.347(6)	15.975(1)
<i>b</i> /Å	12.115(5)	12.136(5)	9.346(3)	15.975(1)
<i>c</i> /Å	18.837(8)	18.968(8)	7.156(2)	21.701(3)
$\beta$ /deg	100.775(6)	99.780(6)	111.551(4)	90
<i>V</i> /Å <sup>3</sup>	2768(2)	2865(2)	1016.9(6)	5538.3(8)
<i>Z</i>	4	4	2	8
<i>D</i> /g cm <sup>−3</sup>	1.701	1.752	1.609	1.547
$\mu$ /mm <sup>−1</sup>	1.151	1.017	1.106	1.138
<i>F</i> (000)	1448	1520	492	2656
reflns measured	7949	8090	2866	13387
obsd reflns	2842	2918	1151	1273
<i>R</i> <sup>a</sup> / <i>wR</i> <sup>b</sup>	0.0590/0.1581	0.0445/0.1290	0.0246/0.0619	0.0797/0.2593

$$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|, \quad ^b wR = [\sum(|F_o|^2 - |F_c|^2)/\sum(F_o^2)]^{1/2}.$$

by weak Ag<sup>+</sup>⋯N interactions between adjacent chains to form a two-dimensional (2D) layer parallel to the crystallographic *bc* plane (Figure 1b). The Ag<sup>+</sup>⋯N distances are 3.736 and 3.433 Å for N1C and N2C (symmetry code C: *x*, *y* − 1, *z*), respectively.

**2.** The structure of complex **2** consists of 1D cationic double chains {[Cu(L<sup>1</sup>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>+</sup>}<sub>*n*</sub> and Cl<sup>−</sup> anions, lattice water, and solvent acetone molecules. The important bond length and angles are listed in Table 2. Each Cu<sup>II</sup> center is six-coordinated by four nitrogen atoms from four different L<sup>1</sup> ligands and two water molecules to form a slightly distorted octahedral geometry. The cis coordination angles vary from 88.20(18) to 91.85(18)°. Four nitrogen donors of ligands lie in the equatorial plane and two coordinated water molecules in the apical positions. The Cu–N distance of 2.009(3) Å is within the range expected for such species. The axial Cu–O distance of 2.428(5) Å is much longer than that of Cu–N, due to the Jahn–Teller effect. In the structure of **2**, two Cu<sup>II</sup> centers are bridged by two L<sup>1</sup> to form a 16-membered macrometallacycle with a Cu⋯Cu separation of 8.575 Å. Each L<sup>1</sup> molecule coordinates to two Cu<sup>II</sup> cations, acting as a bridging ligand to form an infinite 1D cationic double chain structure (Figure 2). Such 1D chains run parallel to each other in the extended lattice. The L<sup>1</sup> ligands coordinate in a propeller-like fashion around the metal, and the dihedral angle between two imidazole rings in one L<sup>1</sup> ligand is 72.1°.

**3 and 4.** **3** and **4** have similar 2D framework structures with only different counterions. All of the figures

are based on **3**. Each Cu<sup>II</sup> ion is coordinated to four imidazole nitrogen atoms from four different L<sup>1</sup> ligands to give a square planar coordination geometry (Figure 3a). Each L<sup>1</sup> ligand links two Cu<sup>II</sup> ions via the aromatic nitrogen atoms, acting as a bridging bidentate ligand. Thus, the Cu<sup>II</sup> centers are connected by L<sup>1</sup> to form 2D networks with (4,4) topology (Figure 3b), which contain 32-membered ring rhombohedral windows with metal ions at each corner and L<sup>1</sup> ligands at each edge. The lengths of all edges are equal with a Cu⋯Cu distance of 8.870 Å for **3** and 8.852 Å for **4**. The fluoroboric or perchlorate counterions are encapsulated in the rhombohedral grid, which may act as templates. The Cu–N distances of 2.000(4) and 2.015(4) Å for **3**; 2.003(3) and 2.015(3) Å for **4** fall in the range of normal Cu–N distances and are similar to those in **2**. The dihedral angle between imidazole rings in one ligand is 108.8° for **3** and 106.4° for **4**, respectively.

**5 and 6.** Complexes **5** and **6** are isostructural; therefore, we use M instead of the Zn and Cd to describe the two complexes. As shown in Figure 4a, each M<sup>II</sup> center is coordinated to six imidazole nitrogen atoms from six different L<sup>1</sup> ligands. The geometry around the M<sup>II</sup> center can be best described as a slightly distorted octahedron with the cis angles ranging from 88.40(9) to 91.60(9)° for **5** and 87.8(3) to 92.3(3)° for **6**. All the M–N bond distances are normal with the average value of 2.199(4) Å for **5** and 2.334(4) Å for **6** (see Table 2).

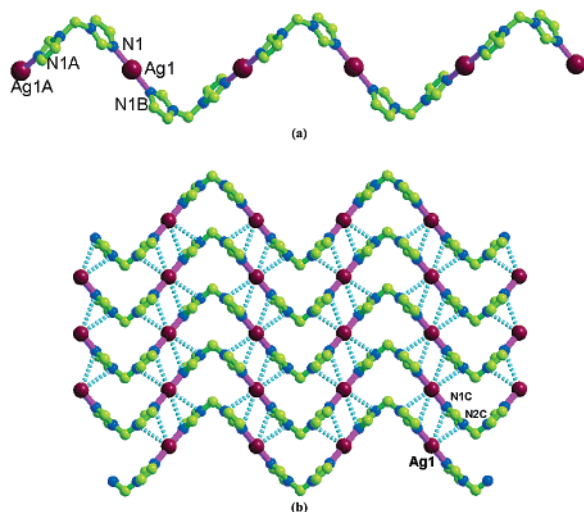
In **5** and **6**, each M<sup>II</sup> ion is connected to other M atoms by two L<sup>1</sup> ligands to form 1D cationic polymeric double



**Table 2.** Selected Bond Lengths (Å) and Angles (°) for Complexes 1–8<sup>a</sup>

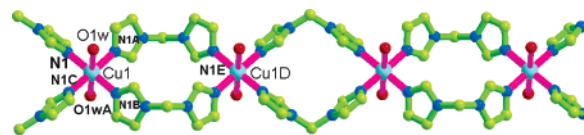
Ag(1)–N(1)	2.093(3)	<b>1</b>	
		N(1) <sup>b</sup> –Ag(1)–N(1)	180
		<b>2</b>	
Cu(1)–N(1)	2.009(3)	Cu(1)–O(1W)	2.428(5)
N(1)–Cu(1)–O(1W)	88.82(10)	N(1)–Cu(1)–N(1) <sup>b</sup>	88.20(18)
N(1)–Cu(1)–N(1) <sup>c</sup>	177.6(2)	N(1) <sup>a</sup> –Cu(1)–O(1W)	91.18(10)
N(1) <sup>a</sup> –Cu(1)–N(1)	91.85(18)	O(1W) <sup>b</sup> –Cu(1)–O(1W)	180.0
		<b>3</b>	
Cu(1)–N(1)	1.999(3)	Cu(1)–N(3)	2.012(3)
N(1)–Cu(1)–N(1) <sup>a</sup>	180	N(1)–Cu(1)–N(3) <sup>a</sup>	92.4(1)
N(1)–Cu(1)–N(3)	87.6(1)		
		<b>4</b>	
Cu(1)–N(1)	2.003(3)	Cu(1)–N(3) <sup>a</sup>	2.015(3)
N(1)–Cu(1)–N(1) <sup>a</sup>	180	N(1)–Cu(1)–N(3) <sup>a</sup>	92.4(1)
N(1)–Cu(1)–N(3)	87.6(1)		
		<b>5</b>	
Zn(1)–N(1) <sup>b</sup>	2.174(4)	Zn(1)–N(5)	2.228(3)
Zn(1)–N(4)	2.195(4)		
N(5) <sup>a</sup> –Zn(1)–N(5)	180	N(5)–Zn(1)–N(4)	91.7(1)
N(5) <sup>a</sup> –Zn(1)–N(1) <sup>b</sup>	89.9(1)	N(1) <sup>c</sup> –Zn(1)–N(4)	91.4(1)
N(5)–Zn(1)–N(1) <sup>b</sup>	90.2(1)	N(5)–Zn(1)–N(4) <sup>a</sup>	88.3(13)
N(4) <sup>a</sup> –Zn(1)–N(4)	180.0	N(1) <sup>c</sup> –Zn(1)–N(4) <sup>a</sup>	88.6(1)
		<b>6</b>	
Cd(1)–N(1) <sup>a</sup>	2.323(4)	Cd(1)–N(5)	2.345(3)
Cd(1)–N(4)	2.335(4)		
N(1) <sup>a</sup> –Cd(1)–N(1) <sup>b</sup>	180	N(1) <sup>b</sup> –Cd(1)–N(4)	91.7(1)
N(1) <sup>a</sup> –Cd(1)–N(5)	90.1(1)	N(4)–Cd(1)–N(5)	92.2(1)
N(1) <sup>a</sup> –Cd(1)–N(4)	88.3(1)	N(4)–Cd(1)–N(5) <sup>c</sup>	87.8(1)
N(1) <sup>b</sup> –Cd(1)–N(5)	89.9(1)	N(5) <sup>c</sup> –Cd(1)–N(5)	180
		<b>7</b>	
Cd(1)–N(1)	2.351(8)	Cd(1)–N(3)	2.326(3)
N(1) <sup>a</sup> –Cd(1)–N(1)	180	N(3)–Cd(1)–N(1) <sup>a</sup>	88.43(7)
N(1) <sup>a</sup> –Cd(1)–N(1) <sup>b</sup>	88.36(9)	N(3)–Cd(1)–N(1)	91.57(7)
N(1) <sup>b</sup> –Cd(1)–N(1)	91.64(9)	N(3) <sup>a</sup> –Cd(1)–N(3)	180
		<b>8</b>	
Zn(1)–N(1)	2.005(4)		
N(1) <sup>a</sup> –Zn(1)–N(1) <sup>c</sup>	103.5(2)	N(1) <sup>a</sup> –Zn(1)–N(1)	112.6(1)

<sup>a</sup> Symmetry codes, for **1**: b,  $-x, -y + 2, -z$ ; for **2**: a,  $-y + 1, -x + 1, -z$ ; b,  $-x + 1/2, -y + 3/2, z$ ; c,  $y - 1/2, x + 1/2, -z$ ; for **3** and **4**: a,  $-x, -y + 1, -z + 1$ ; for **5**: a,  $-x + 1/2, -y + 3/2, -z$ ; b,  $x + 1/2, y + 1/2, z$ ; c,  $-x, -y + 1, -z$ ; for **6**: a,  $x + 1/2, y + 1/2, z$ ; b,  $-x, -y + 1, -z$ ; c,  $-x + 1/2, -y + 3/2, -z$ ; for **7**: a,  $-x - 1, -y - 1, -z + 1$ ; b,  $x, -y - 1, z$ ; for **8**: a,  $y + 1/4, -x + 3/4, -z + 1/4$ , c,  $-y + 3/4, x - 1/4, -z + 1/4$ .

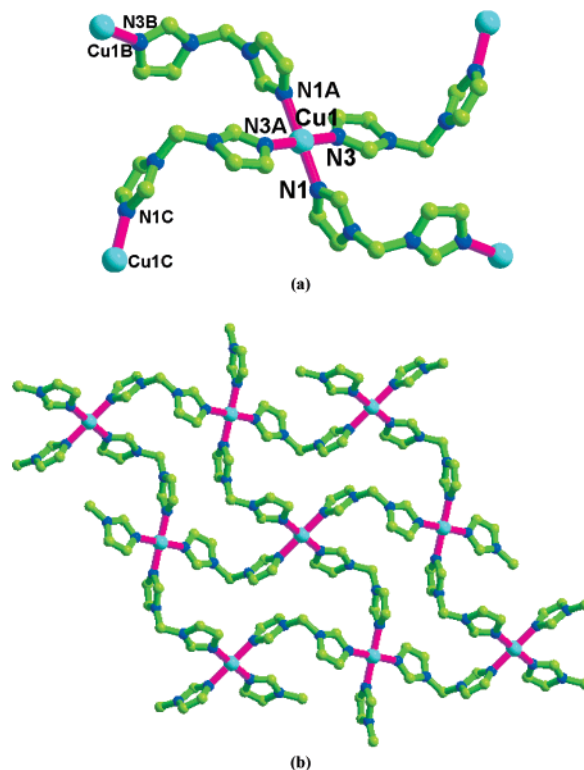
**Figure 1.** (a) A part of the 1D cationic chain in **1** (symmetry codes, A:  $-x, y, 1/2 - z$ ; B:  $-x, 2 - y, -z$ ) and (b) 2D layer structure of **1** assembled by the weak Ag...N interactions (symmetry code, C:  $x, y - 1, z$ ).

Ⓜ 3D-rotatable images of Ⓜ (a) and Ⓜ (b) in WRL format are available.

chains with an adjacent M...M distance of 8.650 Å for **5** and 8.758 Å for **6**. Such chains are arranged nearly

**Figure 2.** The cationic double chain in **2** with 16-membered macrometallacyclic repeating units (symmetry codes, A:  $1/2 - x, 3/2 - y, z$ ; B:  $y - 1/2, 1/2 + x, -z$ ; C:  $1 - y, 1 - x, -z$ ; D:  $x - 1/2, y + 1/2, -z$ ; E:  $1/2 - y, 3/2 - x, z$ ).

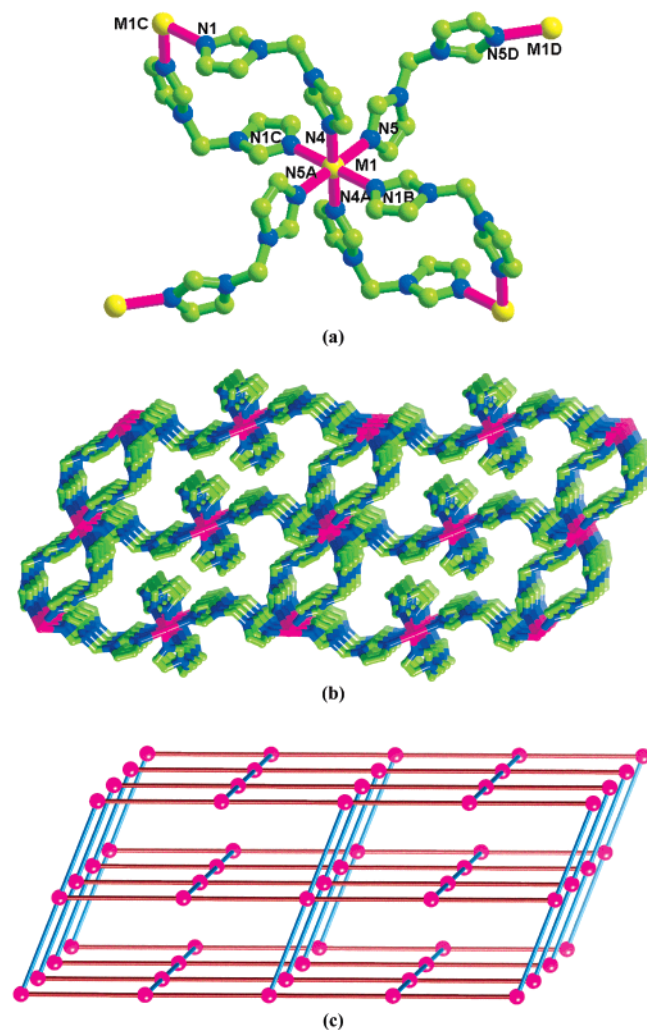
Ⓜ A 3D-rotatable image in WRL format is available.

**Figure 3.** (a) The coordination sphere of the Cu<sup>II</sup> center and the linkage mode of ligands in **3** (symmetry codes, A:  $-x, 1 - y, 1 - z$ ; B:  $x - 1/2, 3/2 - y, z - 1/2$ ; C:  $x - 1/2, y + 1/2, z - 1/2$ ) and (b) the 2D (4,4) network with 32-membered metallo-macrocylic units of **3**.

Ⓜ 3D-rotatable images of Ⓜ (a) and Ⓜ (b) in WRL format are available.

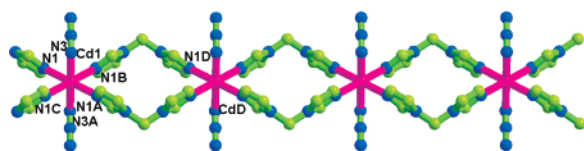
perpendicularly and each M is further linked to two other M atoms by two single L<sup>1</sup> ligands to form a 3D network (M...M separations of 10.251 Å for **5** and 10.464 Å for **6**). Each M<sup>II</sup> ion acts as a square planar 4-connected node, with the overall network topology being that of CdSO<sub>4</sub> (See Figure 4b,c).

**7.** Complex **7** consists of 1D neutral polymeric chains in which the octahedral Cd<sup>II</sup> ion lies on a point of 2/*m* symmetry and is coordinated to four different L<sup>1</sup> ligands and two trans azide ligands. The two trans Cd–N(azide) bond distances [2.326(3) Å] are shorter than the four Cd–N(L<sup>1</sup>) distances [2.352(8) Å], and the cis N–Cd–N bond angles deviate only slightly from *O<sub>h</sub>* symmetry and range from 88.36(9) to 91.57(7)°. Each L<sup>1</sup> connects two Cd<sup>II</sup> ions in the bis-monodentate bridging mode to form a linear 1D neutral polymeric double chain. Two Cd<sup>II</sup> centers are bridged by two L<sup>1</sup> to form a 16-membered metallomacrocycle with a Cd...Cd separation of 9.346 Å (Figure 5), which is longer than the Cu...Cu



**Figure 4.** (a) The coordination modes of the ligands and the center  $\text{Cd}^{\text{II}}$  ions in **5** (symmetry codes, A:  $1/2 - x, 3/2 - y, -z$ ; B:  $1/2 + x, 1/2 + y, z$ ; C:  $-x, 1 - y, -z$ ; D:  $1 - x, y, 1/2 - z$ ), (b) 3D  $\text{CdSO}_4$ -like net of **5** and (c) 3D  $\text{CdSO}_4$ -like topology of **5**.

Ⓜ 3D-rotatable images of Ⓜ (a) and Ⓜ (b) in WRL format are available.

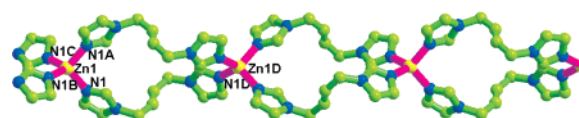


**Figure 5.** A part of the 1D double chain in **7** with 16-membered metallomacrocylic units (symmetry codes, A:  $-1 - x, -1 - y, 1 - z$ ; B:  $x, -1 - y, z$ ; C:  $-x - 1, y, 1 - z$ ; D:  $x, y - 1, z$ ).

Ⓜ A 3D-rotatable image in WRL format is available.

separation in **2**. In the chain structure,  $\text{L}^1$  exhibits a relatively smaller rotation between the two imidazole rings of the ligand than that in **2**, and the corresponding dihedral angle is  $67.8^\circ$ .

Analysis of the crystal packing of **7** shows that such 1D chains are cross-linked by weak hydrogen bonds between nitrogen atoms of the azide anions and the hydrogen atoms of the imidazole ring (in 1 and 2 positions) and methylene group [1:  $\text{C}(1) - \text{H}(5\text{A}) \cdots \text{N}(3)^i$  ( $i = x, y, -1 + z$ ), **2**:  $\text{C}(2) - \text{H}(6\text{A}) \cdots \text{N}(5)^j$  ( $j = -1/2 - x,$



**Figure 6.** A part of the cationic 1D double chain in **8** with the 22-membered macrometallacyclic units (symmetry codes, A:  $1 - x, 1 - y, z$ ; B:  $1/4 + y, 3/4 - x, 1/4 - z$ ; C:  $3/4 - y, x - 1/4, 1/4 - z$ ; D:  $3/4 - y, 3/4 - x, -1/4 - z$ ).

Ⓜ A 3D-rotatable image in WRL format is available.

$1/2 + y, 1 - z$ ) and  $\text{C}(4) - \text{H}(8\text{B}) \cdots \text{N}(5)^{ii}$  ( $ii = -1/2 - x, 1/2 + y, 2 - z$ )). The hydrogen-bonding bond lengths and bond angles are as follows:  $\text{H} \cdots \text{N}$  distances of 2.61, 2.54, 2.39 Å;  $\text{C} \cdots \text{N}$  separations of 3.451, 3.408, 3.345 Å,  $\text{C} - \text{H} \cdots \text{N}$  bonds angles of 150, 155,  $170^\circ$ , being in the normal range of such weak interactions.<sup>8</sup> Such weak interactions extend the 1D chains into a 3D structure. The 1D coordination polymer is extended into higher dimensionality via hydrogen bonds between the 1D systems<sup>9</sup> and not through hydrogen bonds between lattice/coordinated water and/or anions, which provides an interesting example for supramolecular chemistry and crystal engineering.

**8.** To investigate the influence of the length of the ligand spacer on framework formations, complex **8** was obtained by the reaction of  $\text{L}^2$  with  $\text{Zn}(\text{ClO}_4)_2$ . In **8**, the  $\text{Zn}^{\text{II}}$  centers are coordinated by four nitrogen atoms from different  $\text{L}^2$  ligands with a tetrahedron coordination geometry. The  $\text{Zn} - \text{N}(\text{L}^2)$  distance of 2.005(4) Å is shorter than the  $\text{Zn} - \text{N}(\text{L}^1)$  distances in the octahedral arrangement in complex **5**. Each  $\text{L}^2$  coordinates to two  $\text{Zn}^{\text{II}}$  ions though its two aromatic nitrogen atoms acting as a bridging bidentate ligand to form 1D double chains (Figure 6), which are arranged parallel to each other in the crystal. The two  $\text{Zn}^{\text{II}}$  centers are bridged by two  $\text{L}^2$  ligands to form a 22-membered metallomacrocycle with a  $\text{Zn} \cdots \text{Zn}$  separation of 10.851 Å (Figure 6). Each  $\text{L}^2$  ligand has an extended geometry in which the  $\text{N}(\text{CH}_2)_4\text{N}$  chain has an anti configuration and has its plane steeply inclined by 84.5 and  $95.5^\circ$  to the two imidazole rings.

Although  $\text{L}^1$  and  $\text{L}^2$  differ only in the number of  $-\text{CH}_2-$  groups in their alkyl chains, they form quite different metal–organic frameworks with  $\text{Zn}(\text{ClO}_4)_2$ . The former (**5**) has a  $\text{CdSO}_4$ -like 3D framework structure, with six-coordinated octahedron zinc atoms, while the latter (**8**) is a 1D cationic chain with four-coordinated tetrahedron zinc atoms.

In summary, we have obtained eight new complexes with 1D, 2D, or 3D framework structures by self-assembly of two structurally related flexible bis(imidazole) ligands with  $\text{Ag}^{\text{I}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$  salts. The structural differences between **2** and **3** (or **4**), [**6** and **7**] indicate that the counteranions affect the coordination modes of metal and their complex structures.

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**Supporting Information Available:** Crystallographic data for complexes **1–8** in CIF format are available free of charge via the Internet at <http://pubs.acs.org>.

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