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The Tuning Effect of 2-Amino-4,6-dipyridylpyrimidine Isomers on the Structural Dimensionalities and Motifs of Copper(I) Cyanide Complexes

Ying-Nan Chi,[a,b] Feng-Yun Cui,[a,b] Yan-Qing Xu,[a,b] and Chang-Wen Hu*[a,b]

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Four novel copper(I) cyanide complexes of three isomeric oligopyridine ligands, namely 2-amino-4,6-bis(2-pyridyl)pyrimidine (L^1), 2-amino-4-(2-pyridyl)-6-(4-pyridyl)pyrimidine (L^2), 2-amino-4-(2-pyridyl)-6-(3-pyridyl)pyrimidine (L^3) have been hydrothermally synthesized. These complexes have one- and two-dimensional structures, as determined by single-crystal X-ray diffraction. The structural dimensionalities and motifs of complexes **1**–**4** are directed by the coordination modes of the ligands. Thus, L^1 acts as a bis-chelating ligand in complex **1** to join the adjacent 1D $\{CuCN\}_n$ chains into a two-dimensional corrugated layer. Complexes **2** and **4** both consist of one-dimensional zigzag chains where the ligands (L^2 for complex **2** and L^3 for complex **4**) occupy the terminal positions and $N\cdots NH_2$ hydrogen bonds play an important role in the assembly of the supramolecular network. Complex **3** (another product isolated from the L^3-Cu-CN reaction system) is a two-dimensional network in which L^3 acts as a bridging ligand and the cyanide groups exhibit both μ_2 and μ_3 linking modes. Further investigation shows that the thermal stability of complexes **1**–**4** is in the order **1** > **3** > **2** > **4**. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2007)

Introduction

Considerable attention has recently been paid to the crystal engineering of coordination polymers due to their structural and topological novelty[1] and their potential applications in the fields of catalysis, molecular recognition, separation, and nonlinear optics.[2] Although a wide variety of coordination complexes with interesting structures and properties have been reported, it is still a great challenge to control the motifs and dimensionalities of coordination polymers as the formation of these complexes is influenced by many factors, including the coordination behavior of the organic ligand, the solvent system, the metal-to-ligand ratio, the template, and the counteranion.[3] Amongst these factors, the coordination geometry of the organic ligand is very important as, under suitable conditions, the structural information stored in the organic ligand can be read out by the metal ion.[4] This allows the construction of desired architectures by the judicious choice of metal ion and ligand. In this regard, ligand isomers play an important role and sometimes have a tuning effect on the structural dimensionality and motif.[5] A typical case is the bipyridine system, where 4,4′-bipyridine usually acts as a bridging unit to form extended coordination structures with high dimensionalities[6] while 2,2′-bipyridine generally acts as a terminal ligand to form discrete or 1D complexes.[7]

This paper concerns three isomers of 2-amino-4,6-dipyridylpyrimidine, namely 2-amino-4,6-bis(2-pyridyl)pyrimidine (L^1), 2-amino-4-(2-pyridyl)-6-(4-pyridyl)pyrimidine (L^2), and 2-amino-4-(2-pyridyl)-6-(3-pyridyl)pyrimidine (L^3; Scheme 1), and Cu^{II} and CN^- ions for the construction of coordination polymers. The Cu-CN system was selected based on the following considerations. A great deal of attention has been focused on copper cyanide complexes[8] recently because the coordination flexibility of copper ions and the versatile bridging modes of the cyanide ligand make copper cyanide complexes structurally varied.[9] A successful approach employed to develop new metal cyanides is to incorporate bidentate/multidentate organic ligands such as 2,2′-bipyridine or ethylenediamine into the metal-cyanide framework.[10] The structural motifs and dimensionalities of the resultant coordination polymers are often highly influenced by the incorporated ligand.[11] For example, the steric constraints of the introduced ligands and the spatial distances between imine donor groups of the ligands have been shown to have an obvious effect on the structures of Cu-CN complexes.[11a,11c] To the best of our knowledge, however, there is no report of the influence of isomeric ligands on the structure of copper cyanide complexes. Our aim is to understand how the structural motifs and dimensionalities of the Cu-CN coordination polymers can be manipulated by the ligand isomers.

Ligands L^1–L^3 are pentadentate, multifunctional ligands. The coordination chemistry of these ligands has not been

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[a] The Institute for Chemical Physics, and Department of Chemistry, Beijing Institute of Technology,
Beijing 100081, P. R. China
[b] State Key Labarotory of Explosion Science and Technology, Beijing Institute of Technology,
Beijing, 100081, P. R. China
Fax: +86-10-68914780
E-mail: cwhu@bit.edu.cn

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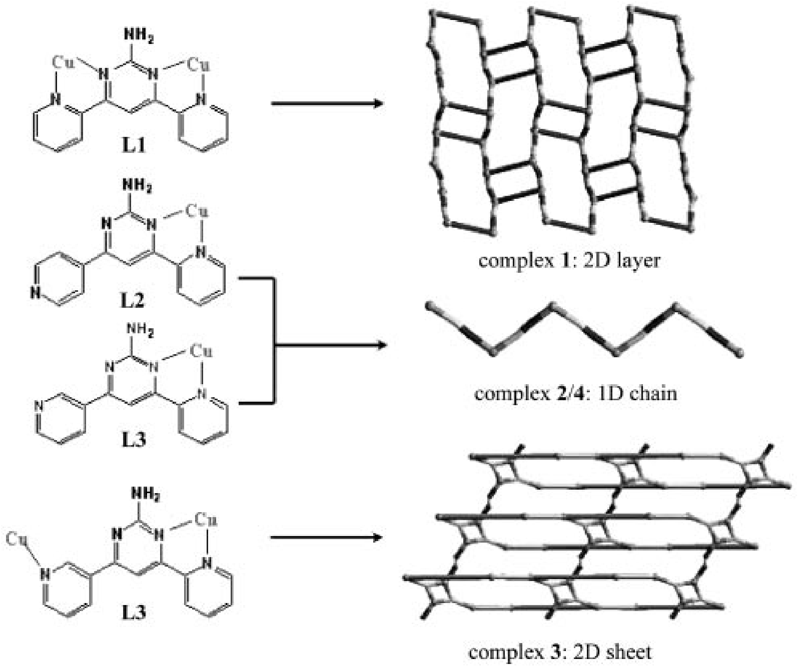

Scheme 1. The coordination modes of the three ligand isomers L^1–L^3 in complexes **1**–**4** and their resultant structural motifs.

explored widely to date, except for a few silver(I) and copper(I/II) complexes reported by us recently.[12] We found that the structures of these complexes are directed by the counteranions and ligand isomerism. Every isomer has a bidentate binding site that is capable of chelating one metal center, but the different pyridine substituent groups at the 6-position of the pyrimidine ring make them exhibit different coordination modes, which probably have a large influence on the resultant structures. In addition, the three isomers possess hydrogen-bond donor (amino group) and acceptor (aromatic N atoms) groups, which could be available for the formation of an H-bond network.

Herein we report four new copper-cyanide coordination polymers, namely $[Cu_2(CN)_2L^1]_n$ (**1**), $[CuCNL^2]_n$ (**2**), $[Cu_3(CN)_3L^3]_n$ (**3**), and $[CuCNL^3]_n$ (**4**), in all of which Cu^{II} has been reduced to Cu^{I} under the hydrothermal conditions used. The dimensionalities of complexes **1**–**4** vary with the coordination modes of the ligands (Scheme 1) and complexes **2** and **4** have the same molecular formula and different structures. These complexes not only enrich the structural database of copper(I) cyanide complexes but also demonstrate the tuning effect of ligand isomerism upon the dimensionalities and motifs of the resultant crystal structures.

Results and Discussion

Synthesis

Solvothermal reactions have recently been demonstrated to be a versatile technique for the construction of coordination polymers, and a large number of cyanide complexes have been synthesized by this method. We chose $K_3[Fe(CN)_6]$ as the source of cyanide anions because cyanide ions are slowly released from this complex under hydrothermal condition. Several kinds of Cu^{II} salts [$CuCl_2\cdot 2H_2O$, $CuBr_2$, $Cu(NO_3)_2\cdot 3H_2O$, $Cu(OOCCH_3)_2\cdot H_2O$] were investigated but they were found to only act as a copper source and the counteranions are not involved in the crystal structures. Moreover, the Cu^{II} ions are reduced to Cu^{I} in all four complexes. This observation is consistent with the fact that copper(I) cyanide species are more stable than copper(II) complexes at elevated temperatures and pressures.[13] The cyanide groups obtained from the dissociation of $[Fe(CN)_6]^{3-}$ are probably responsible for the reduction process, yielding cyanogen as the oxidation product.

To investigate the influence of the reaction conditions we varied the metal/ligand ratio, reaction time, and temperature. Formation of complexes **1** and **2** is not obviously affected by the metal/ligand ratio ($CuCl_2/K_3[Fe(CN)_6]/L$ = 1:1:1, 1:2:1, 2:1:1, and 2:1:2), reaction time (24, 48, and 72 h), or temperature (120, 140, 160, 180 °C), although the yields did vary somewhat. However, the reaction conditions have a tuning effect on the final product obtained from the reaction between L^3, Cu^{II}, and $K_3[Fe(CN)_6]$. Thus, when the reaction was run with a molar ratio of 1:2:1 at 160 °C for 72 h the dominant product was complex **4**, whereas complex **3** was isolated in high yield with a 2:1:1 ratio. Similarly, when the same reaction with a 1:1:1 molar ratio was carried out at 160 °C for 24 h **4** was the only product, whereas after 48 or 72 h both complexes **3** and **4** both were obtained with different yields. When reactions with a 1:1:1 molar ratio were performed at 120 °C for 72 h only complex **4** was formed, whereas at 180 °C complex **3** was isolated as a pure phase and at 140 and 160 °C both complexes **3** and **4** were formed. On the basis of the above results we can conclude that increasing the temperature or extending the reaction time is beneficial to the formation of **3**, therefore careful control of the reaction conditions allows us to obtain the desired product.

The coordination modes of ligands L^1–L^3 and the structural motifs of complexes **1**–**4** are summarized in Scheme 1. The structure of complex **1** consists of a wave-like layer in which CN groups link the Cu^I ions to form a 1D $\{CuCN\}_n$ chain and L^1 acts as a bis-chelating ligand to bridge adjacent chains. Complexes **2** and **4** contain a zigzag chain that is unable to propagate to higher dimensionality, probably due to the terminal coordination mode of L^2/L^3. The structure of complex **3** is a 2D sheet in which the CN groups exhibit both μ_2 and μ_3 bridging modes and L^3 binds two metal centers, one through the N atoms in a chelating mode and the other through the N atom on the 3-pyridine ring. We suppose that the different coordination modes adopted by the ligand isomers, in combination with the versatile linking behavior of the cyanide groups, is responsible for the diversity of the structures reported.

IR Spectroscopy

The IR bands corresponding to the CN stretching vibrations for complexes **1**–**4** appear in the range 2099–2123 cm^{-1}, which is typical for bridging cyanide groups and higher than that of terminal cyanide groups (approx. 2050 cm^{-1}).[14] The IR spectra of complexes **2** and **4** exhibit one ν(CN) stretching band at 2107 (for **2**) and 2099 (for **4**) cm^{-1}, which is in agreement with the presence of only one type of cyanide, while complexes **1** and **3** exhibit two stretching bands, thus indicating the existence of two types of cyanide bridges in the structure. The cyanide groups in the crystal structure of complex **3** exhibit μ_2 and μ_3 bridging modes but for complex **1** there is only one type of μ_2-CN group, therefore the presence of two stretching bands for the latter might originate from the subtle difference of the Cu^I–N bond lengths [1.981(4) and 1.952(3) Å]. A similar phenomenon has been observed in other cyanide complexes.[11d,15] The absorption peaks between 3460 and 3280 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of the NH$_2$ group, and the absorption peaks below 1700 cm^{-1} are mainly attributed to the vibrations of the aromatic rings.

X-ray Crystal Structures

Complex 1

The structure of complex **1** can be described as a neutral non-interpenetrating corrugated sheet containing two different types of copper(I) centers (Figure 1), both of which coordinate to two N atoms from L^1 and two cyanide groups and exhibit distorted tetrahedron geometries. L^1 acts as a bis-chelating ligand bridging two metal centers, as observed previously in silver(I) complexes of L^1.[12] The Cu–N$_{aryl}$ bond lengths fall in a narrow range [2.082(3)–2.112(3) Å] and the Cu–$C_{cyanide}$ bond lengths [Cu1–C16 = 1.886(4), Cu2–C15A = 1.885(4) Å] are very similar. The Cu–N$_{cyanide}$ distances [Cu1–N6 = 1.981(4), Cu2–N7A = 1.952(3) Å], however, are different. The acute angles at the chelating sites of L^1 [77.20(11)° for N1–Cu1–N4 and 77.23(10)° for N2–Cu2–N5] are responsible for the distorted tetrahedral geometries of the copper centers. In this case, the dihedral angles between the pyrimidine ring and two pyridine rings are 2.0° and 5.2°, respectively, and that between the two pyridine rings is 6.5°. All the dihedral angles in complex **1** are clearly smaller than those observed in Ag^{I}L^1 complexes.[12]

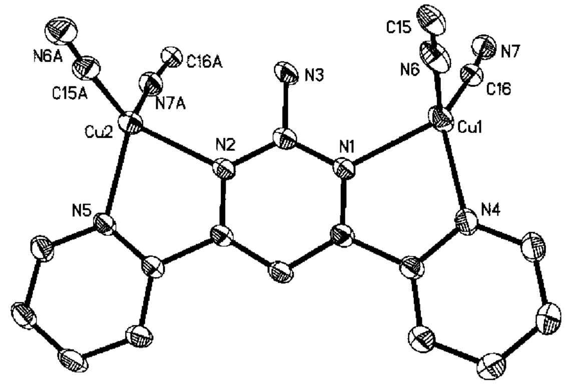

Figure 1. Coordination environments of the Cu ions in complex **1**. All H atoms have been omitted for clarity. Symmetry codes: (A) $5/2 - x, -1/2 + y, 3/2 - z$; (B) $2 - x, -y, 2 - z$.

As shown in Figure 2, the structure of **1** is constructed from zigzag $\{CuCN\}_n$ chains running along the *c*-axis that are linked together by the L^1 ligands to generate a 4.8(2) network (Figure S1 in the Supporting Information). Interestingly, the sheet contains two kinds of rings: a 16-membered Cu$_4$(CN)$_2$(L^1)$_2$ ring A and a 26-membered Cu$_8$(CN)$_6$(L^1)$_2$ ring B. This means that the structure can also be described as a layer composed of A and B rings. In ring A, the distance between two Cu atoms chelated by the same L^1 ligand is 6.154 Å, and two Cu atoms separated by a cyanide group are 4.930 Å apart. In general, 2D networks

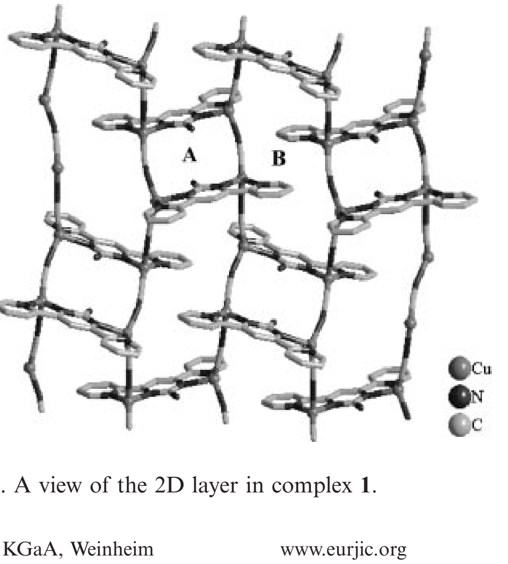

Figure 2. A view of the 2D layer in complex **1**.

in the Cu-CN system are generated by the linking of 1D $\{CuCN\}_n$ chains by linear dipodal ligands such as 4,4′-bipyridine, 2,2′-bipyrimidine, pyrazine, etc., and these networks usually only include one kind of ring unit.[7a,10c,11c] The 2D net observed in **1**, however, consists of two types of rings (A and B), and we believe that the non-linear bridging mode of L^1 is responsible for this special motif. The 2D sheets are stacked in an ABAB pattern and are assembled into a 3D supramolecular structure by π–π interactions between the L^1 ligands, with a plane-to-plane distance of about 3.55 Å (Figure S2).

Complex 2

The cyanide groups in **2** connect the copper(I) anions to form a neutral zigzag chain along the *b*-axis with the L^2 ligands hanging from the metal centers (Figure 3). The asymmetric unit in **2** contains one copper center, one cyanide group, and one L^2 ligand. The copper ion is coordinated by two cyanide groups and two nitrogen atoms from L^2 with a distorted tetrahedral geometry. Ligand L^2 does not adopt the bridging mode previously found in Ag^IL^2 and Cu^IL^2 complexes but acts as a terminal ligand that binds through the chelating N atoms. The N5 atom on the 4-pyr-

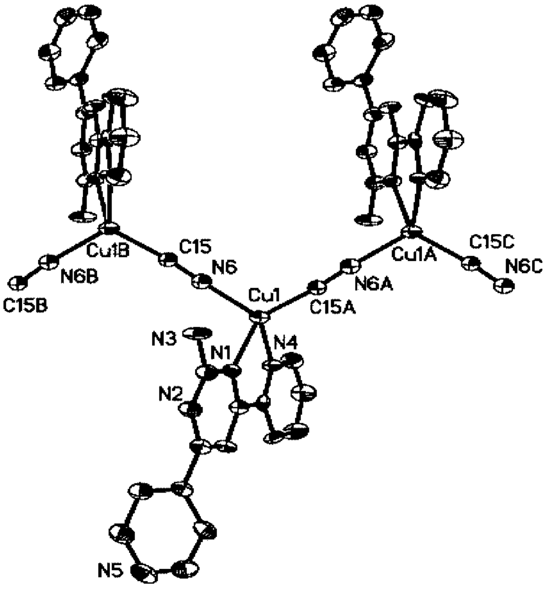

Figure 3. The 1D zigzag chain of complex **2**. All H atoms have been omitted for clarity. Symmetry codes: (A) *x*, –1/2 + *y*, 1/2 – *z*; (B) *x*, 1/2 + *y*, 1/2 – *z*; (C) *x*, –1 + *y*, *z*.

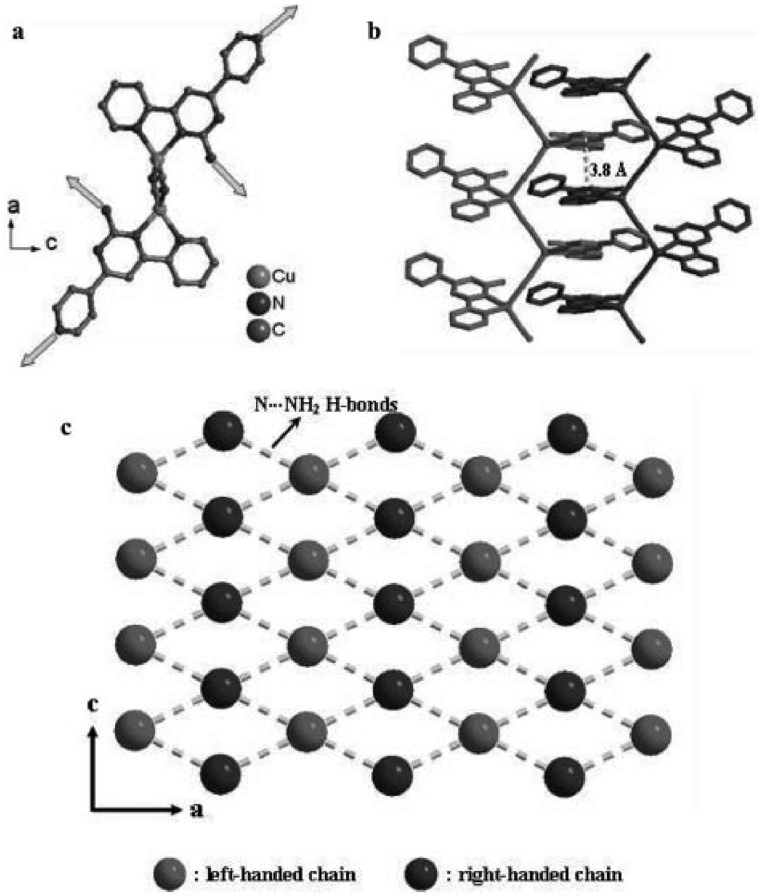

Figure 4. (a) A side view of the zigzag chain of complex **2** projected along the *b*-axis. The arrows represent the directions along which the 1D chain forms H-bonds with four neighboring chains. (b) Two differently orientated chains with π–π interactions in complex **2**. (c) A schematic presentation of the 3D supramolecular structure of complex **2**.

idine ring does not participate in coordination and points away from the zigzag chain. The Cu–N_{py} [2.094(4) Å] and Cu–N_{pym} [2.090(3) Å] bond lengths are rather similar and the acute angle at the chelating site of L^2 [78.2(3)° for N1–Cu1–N4] accounts for the obviously distorted geometry of the copper ion. The bond lengths involving the cyanide group [Cu1–C6 = 1.874(5), Cu1–N15A = 1.965(4), C15–N6 = 1.148(5) Å] are similar to those found in other copper cyanide complexes.[16] The shortest Cu···Cu distance within the chain is 4.949 Å and the shortest interchain Cu···Cu distance is 6.814 Å. The pyrimidine and 2-pyridine rings are nearly coplanar (dihedral angle of 2.4°) while the 4-pyridine ring lies outside of this plane. The dihedral angle between the 4-pyridine and pyrimidine rings is 23.5° and that between the 4-pyridine and 2-pyridine rings is 24.2°.

Neighboring chains in this structure have different orientations (Figure 4, b) and the L^2 ligands from two adjacent chains are stacked in an offset fashion with a plane-to-plane distance of 3.8 Å, thus indicating weak π–π interactions. For clarity, one is referred to as the left-handed chain and the other the right-handed chain. A projected view of the zigzag chain shows that the N atoms of the 4-pyridine and amino groups point in four different directions (Figure 2, a), and every chain forms H-bonds (N···NH_2 = 3.041 Å; H–N···N = 150.17°) with four neighboring chains along these four directions. The more interesting observation is that each left-handed chain connects to four adjacent right-handed chains, and vice versa (Figure 4, c and Figure S3, Supporting Information). The isolated zigzag chains are therefore assembled into a 3D supramolecular structure by H-bonds. The H-bond interaction is an important element in the construction of supramolecular structure, but seldom appears in Cu CN complexes.[9c,16] In this case, the successful formation of H-bonds is due to the L^2 ligand containing both an H-bond acceptor (N5) and donor (NH_2).

Complex 3

The presence of ligand L^3 results in a 2D sheet in **3**. As shown in Figure 5 (a), there are three different metal centers (Cu1, Cu2, Cu3) in the asymmetric unit of **3**, all of which are three-coordinate with distorted trigonal geometries. The detailed coordination environments of the three Cu atoms are different. Cu1 is coordinated to three N atoms from two cyanide groups and one L^3 ligand with N–Cu–N bond angles varying from 102.6(5)° to 148.2(5)°, Cu2 is ligated to two N atoms from the chelating site of L^3 and one cyanide group, with the bond angles around Cu^I ranging from 80.5(3)° to 145.8(4)°, while Cu3 is coordinated by three cyanide groups, with bond angles in the range 107.6(6)°–131.6(7)°. The Cu–N_{aryl} bond lengths range from 2.052(11)

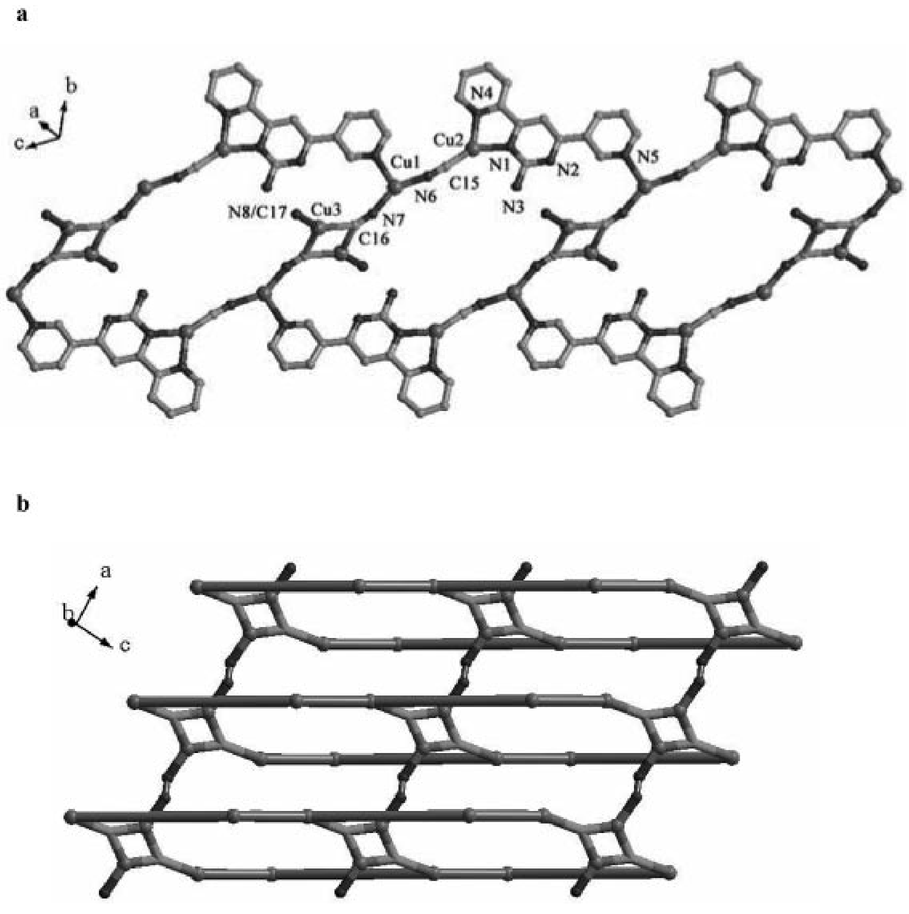

Figure 5. (a) The staggered ladder in complex **3**. All H atoms have been omitted for clarity. (b) A schematic presentation of the 2D sheet of complex **3**.

to 2.158(12) Å and the Cu–N/C_{cyano} bond lengths are in the range 1.930(13)–2.210(19) Å. L^3 acts as a bridging ligand linking two copper centers. The three aromatic rings of L^3 are nearly in the same plane, with dihedral angles ranging from 2.3° to 3.6°. All the dihedral angles observed in complex **3** are smaller that those in complexes **1** and **2**.

The cyanide groups in **3** exhibit both μ_2- and μ_3-bridging modes. Two μ_3-cyanide groups bond link two Cu3 centers through their carbon atoms to form a $Cu_2(CN)_2$ unit that includes a Cu_2C_2 rhombic ring with a Cu···Cu distance of 2.532 Å. The $Cu_2(CN)_2$ unit is a familiar motif in complexes containing μ_3-cyanide and reported cases almost all have a short $Cu^I\cdots Cu^I$ distance of between 2.42 and 2.66 Å.[8c,11c,11d,17] As shown in Figure 5 (a), two $Cu_2(CN)_2$ units, two μ_2-cyanide groups, two L^3 ligands, and six copper ions are assembled into a 40-membered ring in which the largest Cu···Cu distance is 22.006 Å, the distance between two Cu atoms chelated by the same L^3 ligand is 9.865 Å, and two Cu atoms separated by a $Cu_2(CN)_2$ unit are 9.430 Å apart. Two ligands lie parallel to each other in the macrocycle with the amino groups pointing towards the center of the ring. Adjacent rings are fused along the edges containing the $Cu_2(CN)_2$ unit to form a ribbon. Alternatively, the ribbon may be described as a staggered ladder with $\{CuL^3(CN)\}_n$ chains as the side-rails and $Cu_2(CN)_2$ units as the rungs. For clarity, the staggered ladder can be simplified with the Cu atoms as nodes and L^3 ligands and μ_2-cyanide groups as linkers (Figure S4). The rhombic rings of $Cu_2(CN)_2$ units are almost perpendicular to the ladder and the Cu3 atoms point to opposite sides. The disordered μ_2-cyanide groups link the Cu3 centers from adjacent 1D ladders to generate a 2D sheet along the *a*-axis (Figure 5, b). The shortest Cu···Cu distance between adjacent sheets is 3.084 Å.

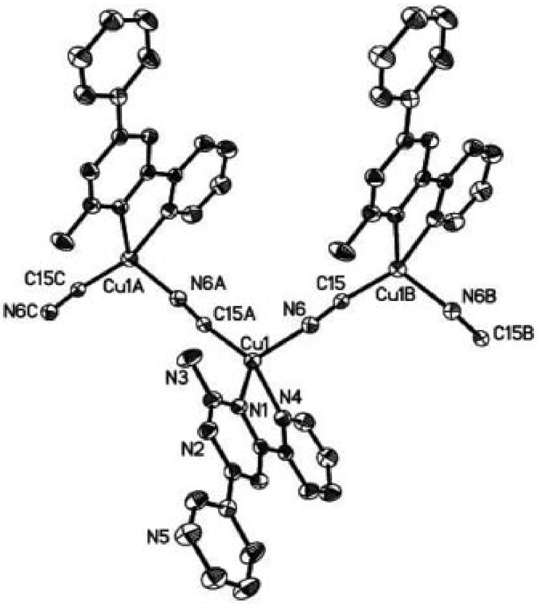

Figure 6. The 1D zigzag chain of complex **4**. All H atoms have been omitted for clarity. Symmetry codes: (A) *x*, 1/2 – *y*, –1/2 + *z*; (B) *x*, 1/2 – *y*, 1/2 + *z*; (C) *x*, *y*, –1 + *z*.

Complex 4

Complex **4** is a 1D zigzag chain extending along the *c*-axis. As shown in Figure 6, there is only one kind of copper center in **4**, which is four-coordinated by two N atoms from L^3 and two cyanide groups and adopts a distorted tetrahedron geometry. The bond lengths around Cu^I range from 1.884(3) to 2.099(2) Å and the bond angles are in the range 77.84(9)–119.76(11)°. Ligand L^3 does not adopt the bridging mode observed in **3** in this complex but acts as a terminal ligand. The pyrimidine and 2-pyridine rings are almost in the same plane, with a dihedral angle of about 0.8°, and the dihedral angles between pyrimidine and the 2-pyridine and 3-pyridine rings are about 3.1° and 3.9°, respectively. The dihedral angles observed in this crystal are obviously smaller than those in complex **2**. The shortest intrachain Cu···Cu distance is 5.011 Å and the shortest interchain Cu···Cu distance is 5.494 Å.

Complexes **2** and **4** have the same molecular formula and their structures are also very similar. However, a side view

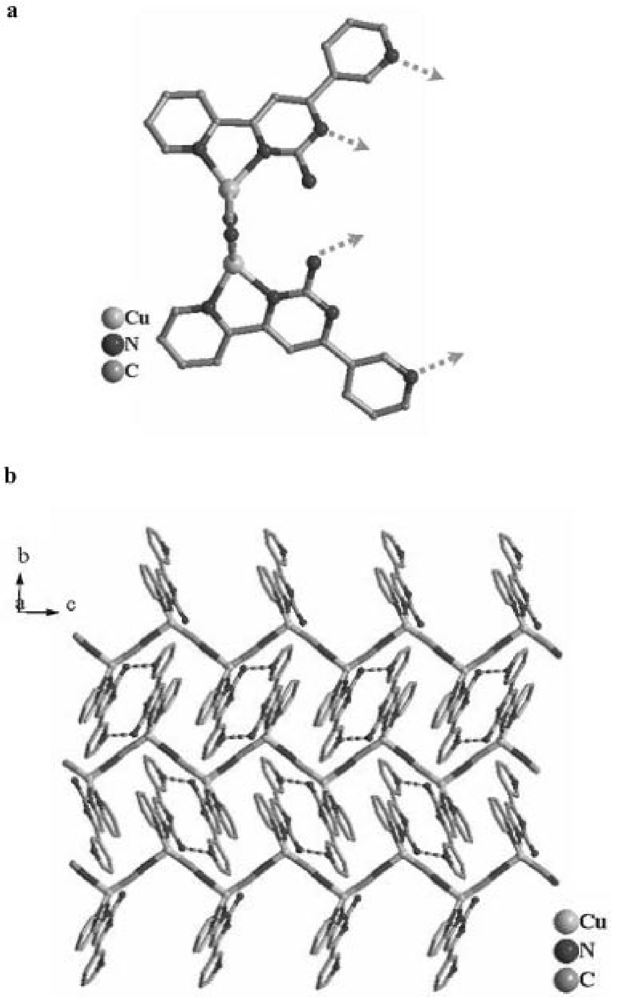

Figure 7. (a) A side view of the zigzag chain in complex **4** projected along the *c*-axis. The dashed arrows represent the directions along which the 1D chain forms H-bonds with two neighboring chains. (b) The 2D supramolecular network in complex **4** assembled by H-bonds. The dashed lines represent the H-bond interactions.

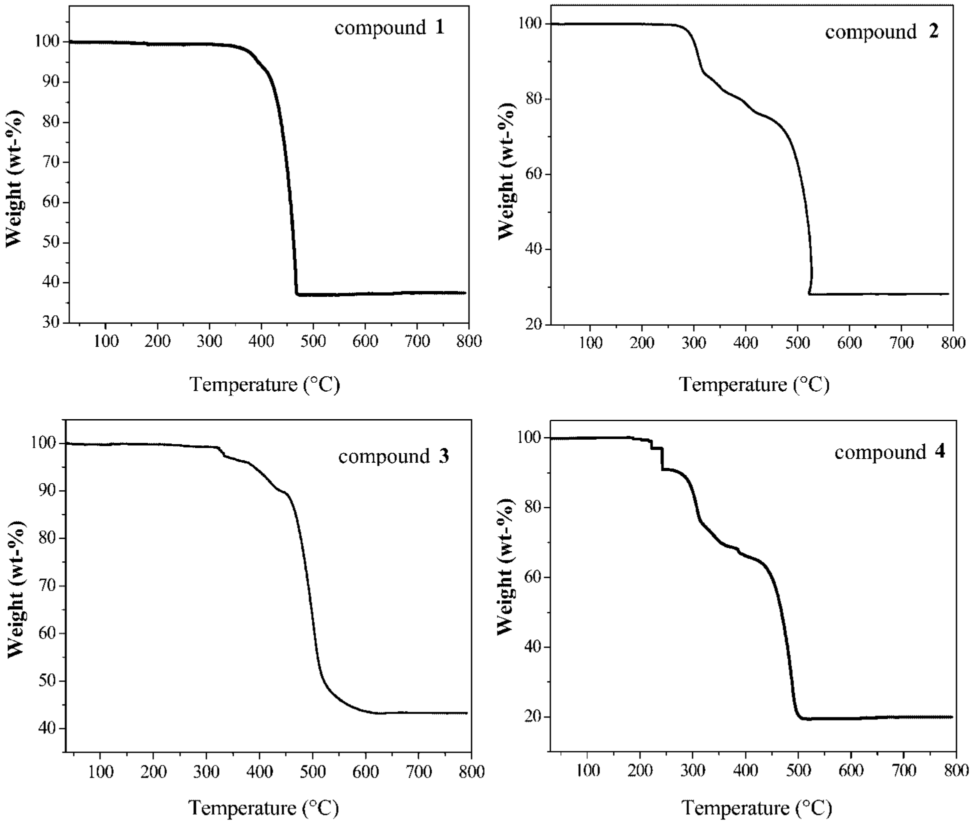

Figure 8. The TG curves of complexes **1**–**4**.

(see parts a in Figures 4 and 7) shows clearly that the orientation of the ligands in the two structures is different. Thus, the L^2 ligands are located on the two sides of the chain with the amino groups and the N atoms of the 4-pyridine rings pointing in four different directions in complex **2**, whereas in complex **4** the L^3 ligands are nearly oriented on the same side and the amino groups and the uncoordinated N atoms on the 3-pyridine rings point in only two different directions. As in complex **2**, the neighboring chains of **4** have different orientations and are linked together by H-bonds (N···N 2.980 Å; N–H···N 158.53°) between the NH_2 and N5 atoms to form a 2D supramolecular network (Figure 7, b). These 2D layers are assembled into a 3D supramolecular framework by π–π interactions between the pyrimidine and 2-pyridine rings (plane-to-plane distance of approx. 3.5 Å).

Interestingly, complexes **3** and **4**, which have distinct structural motifs and dimensionalities, were isolated from the same reaction system. We think that the structural diversity of the Cu/CN/L^3 system originates from the flexible and adjustable coordination modes of ligand L^3. To the best of our knowledge, this case represents the first example where two Cu-CN coordination polymers are obtained from the same reaction system.

Thermal Stability

The thermal stability of complexes **1**–**4** was determined by TG analysis (Figure 8). Complex **1** is stable from room temperature up to 350 °C. It then undergoes a total weight loss of 63.02% (calculated value: 64.01%), corresponding to one L^1 ligand and one cyanide group, in the range 350–570 °C. Complex **2** shows a two-step weight loss between 275 and 500 °C. The total weight loss of **2** is 72.14% (calculated value: 73.41%), which corresponds to one ligand L^2. The weight loss for complex **3** between 320 and 600 °C is 57.99% (calculated value: 56.67%), which corresponds to one L^3 ligand and one cyanide group. The total weight loss for complex **4** between 200 and 500 °C is 80.56% (calculated value: 81.12%), which corresponds to one L^3 ligand and one cyanide group. The thermal stability of complexes **1**–**4** follows the order **1** (350 °C) > **3** (320 °C) > **2** (275 °C) > **4** (200 °C). These results are consistent with the above structural analysis and confirm that the high-dimensional networks (**1** and **3**) are more stable than the low-dimensional chains (**2** and **4**), and, for the 1D polymers, that the 3D H-bonded supramolecular structure (**2**) is more stable than the 2D supramolecular structure (**4**).

Conclusions

Four novel copper(I) complexes, **1**–**4**, have been successfully prepared under hydrothermal condition by using three isomeric ligands L^1, L^2, and L^3 in combination with cyanide groups. L^3 is a new compound and, to the best of our knowledge, ligands L^1, L^2, and L^3 are employed here in the copper cyanide system for the first time. Ligands L^2 and L^3

in complexes **2** and **4** act as terminal ligands to form a 1D structure, while the two-dimensional networks of **1** and **3** are constructed from L^1 and L^3 exhibiting different bridging modes. The above results indicate that the coordination modes adopted by ligand isomers L^1, L^2, and L^3 have a tuning effect on the structural motifs and dimensionalities of the coordination polymers. Further investigation of the role of these three isomeric ligands in other transition metal systems is in progress.

Experimental Section

General Remarks: All copper(II) salts were purchased from commercial sources and used without further purification. Organic solvents with analytical purity were supplied by commercial sources and used as received. Infrared spectra were recorded (as KBr pressed pellets) with a Nicolet 170SXFT/IR spectrometer. ^{1}H NMR spectra (for L^3) were recorded with a Bruker DPX 500 spectrometer. X-ray powder diffraction (XPRD) patterns were collected with a Japan Rigaku D/max γA X-ray diffractometer equipped with graphite-monochromated Cu-K_α radiation (λ = 0.154060 nm). Elemental analyses were performed with a Perkin–Elmer 2400 CHN elemental analyzer. TG analyses were carried out in air between 30 and 800 °C at a heating rate of 10 °C min^{-1} with a 2960 SDT simultaneous thermal analyzer.

Synthesis of L^1, L^2, and L^3: The ligands L^1, L^2, and L^3 were prepared according to previously reported synthetic procedures.[18] The synthesis of L^3 was similar to that of ligands L^1 [18] and L^2.[12a] Data for L^3: Yield: 63%; m.p. 182–184 °C. ^{1}H NMR (CDCl$_3$, 500 MHz, 25 °C): δ = 9.35 (s, 1 H, 2-pyridyl), 8.74–8.71 (m, 2 H, pyridyl), 8.43–8.39 (m, 2 H, pyridyl), 8.17 (s, 1 H, pyrimidyl), 7.88–7.86 (m, 1 H, pyridyl), 7.44–7.40 (m, 2 H, pyridyl), 5.24 (s, 2 H, amino group) ppm. IR (KBr): $\tilde{\nu}$ = 3329 (m), 3197 (m), 3055 (w), 2991 (w), 1650 (s), 1575 (s), 1564 (s), 1478 (s), 1433 (w), 1365 (s), 1238 (m), 1133 (w), 1092 (w), 994 (w), 845 (w), 781 (s), 743 (w), 706 (m), 661 (w), 623 (w) cm^{-1}.

Synthesis of $[Cu_2(CN)_2L^1]_n$ (1): A mixture of L^1 (24.9 mg, 0.1 mmol), $CuCl_2\cdot 2H_2O$ (16.9 mg, 0.1 mmol), $K_3[Fe(CN)_6]$ (32.8 mg, 0.1 mmol), and H_2O (8 mL) was transferred and sealed in a 15-mL Teflon-lined stainless steel autoclave, which was heated to 160 °C for 72 h and then cooled to room temperature. Red-brown cubic crystals were collected for X-ray analysis. Yield: 39.1 mg (91%, based on L^1). $C_{16}H_{11}Cu_2N_7$ (428.4): calcd. C 44.86, H 2.59, N 22.89; found C 44.92, H 2.67, N 22.78. IR (KBr): $\tilde{\nu}$ = 3460 (s), 3349 (s), 3096 (w), 3059 (w), 2112 (s), 2101 (s), 1732 (w), 1596 (s), 1583 (s), 1540 (s), 1456 (m), 1421 (m), 1370 (m), 1305 (m), 1240 (s), 1169 (w), 1156 (w), 1055 (w), 1007 (w), 852 (m), 791 (s), 772 (s), 737 (m), 664 (m) cm^{-1}.

Synthesis of $[CuCNL^2]_n$ (2): Complex **2** was synthesized in a manner similar to that used to obtain complex **1**, but with L^2 as ligand. Red-brown stick crystals were collected for X-ray analysis. Yield: 28.8 mg (85%, based on L^2). $C_{15}H_{11}CuN_6$ (338.8): calcd. C 53.17, H 3.27, N 24.80; found C 53.11, H 3.36, N 24.89. IR (KBr): $\tilde{\nu}$ = 3422 (m), 3298 (m), 3182 (w), 3066 (w), 2107 (s), 1624 (s), 1583 (s), 1547 (s), 1500 (w), 1470 (m), 1414 (m), 1373 (s), 1257 (w), 1230 (m), 1066 (w), 998 (w), 830 (s), 785 (s), 743 (w), 650 (m), 631 (m) cm^{-1}.

Synthesis of $[Cu_3(CN)_3L^3]_n$ (3): Complex **3** was synthesized at 180 °C in a manner similar to that used to obtain complex **1**, but with L^3 as ligand. Dark red crystals were collected for X-ray analysis. Yield: 19.4 mg (41%, based on L^3). $C_{16.5}H_{11}Cu_{2.5}N_{7.5}$ (473.2): calcd. C 41.88, H 2.34, N 22.20; found C 41.94, H 2.42, N 22.29. IR (KBr): $\tilde{\nu}$ = 3615 (w), 3443 (w), 3358 (m), 3059 (w), 2924 (w), 2123 (s), 2101 (s), 1592 (s), 1539 (s), 1478 (s), 1449 (s), 1420 (m), 1367 (s), 1257 (w), 1232 (m), 1200 (w), 1143 (w), 1049 (w), 1028 (w), 1016 (w), 778 (s), 701 (m), 660 (m), 640 (w) cm^{-1}.

Synthesis of $[CuCNL^3]_n$ (4): A mixture of L^3 (24.9 mg, 0.1 mmol), $CuCl_2$ (16.9 mg, 0.1 mmol), $K_3[Fe(CN)_6]$ (65.6 mg, 0.2 mmol), and H_2O (8 mL) was transferred and sealed in a 15-mL Teflon-lined stainless steel autoclave, which was heated to 160 °C for 72 h and then cooled to room temperature. Brown cubic crystals were collected for X-ray analysis. Yield: 30.2 mg (89%, based on L^3). $C_{15}H_{11}CuN_6$ (338.8): calcd. C 53.17, H 3.27, N 24.80; found C

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

	1	2	3	4
Formula	$C_{16}H_{11}Cu_2N_7$	$C_{15}H_{11}CuN_6$	$C_{16.5}H_{11}Cu_{2.5}N_{7.5}$	$C_{15}H_{11}CuN_6$
Fw	428.40	338.84	473.18	338.84
a [Å]	11.127(2)	16.528(15)	7.72(4)	11.743(3)
b [Å]	12.274(2)	8.168(8)	9.76(5)	15.539(4)
c [Å]	12.334(2)	21.62(2)	12.21(6)	8.085(2)
α [°]	90	90	97.85(7)	90
β [°]	92.299(3)	90	94.85(6)	98.038(3)
γ [°]	90	90	90.85(6)	90
Space group	$P2_1/n$	*Pbca*	$P\bar{1}$	$P2_1/c$
D_{calc} [Mg m^{-3}]	1.691	1.542	1.731	1.541
Z	4	8	2	4
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Volume [Å^3]	1683.1(6)	2910(2)	908(8)	1460.8(7)
F(000)	856	1376	470	688
Crystal size [mm]	0.33 × 0.21 × 0.14	0.65 × 0.21 × 0.04	0.43 × 0.21 × 0.19	0.37 × 0.34 × 0.25
Reflections collected	8620	14078	4125	7380
Unique reflections	2966	2576	2903	2572
Goof	1.048	0.948	0.981	1.074
$R1$ [$I > 2\sigma(I)$][a]	0.0325	0.0492	0.0762	0.0330
$\omega R2$ [$I > 2\sigma(I)$]	0.0734	0.0953	0.1990	0.0802
$R1$ (all data)	0.0520	0.1102	0.1524	0.0562
$\omega R2$ (all data)	0.0840	0.1152	0.2628	0.0982

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

53.23, H 3.34, N 24.72. IR (KBr): $\tilde{\nu}$ = 3398 (m), 3284 (w), 3108 (m), 2099 (s), 1633 (s), 1588 (s), 1547 (s), 1461 (s), 1420 (m), 1363 (s), 1232 (m), 1192 (w), 1143 (w), 1057 (w), 1024 (m), 844 (w), 824 (m), 779 (s), 742 (m), 705 (m), 664 (m), 551 (m), 431 (w) cm^{-1}.

X-ray Crystallographic Analysis: Suitable single crystals of complexes **1**–**4** were mounted on a Bruker-AXS CCD diffractometer equipped with a graphite-monochromated Mo-K_α radiation source (λ = 0.07103 Å) at 298 K. All absorption corrections were performed with the SADABS program. All the structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in the calculated positions. All calculations were performed using the SHELXTL-97 program.[19] The crystallographic details of complexes **1**–**4** are summarized in Table 1. Selected bond lengths and angles of complexes **1**–**4** are listed in Table 2.

Table 2. Selected bond lengths [Å], angles [°], and other distances for **1**–**4**.[a]

Complex **1**			
Cu(1)–C(16)	1.886(4)	N(4)–Cu(1)–N(1)	77.20(11)
Cu(1)–N(6)	1.981(4)	C(16)–Cu(1)–N(6)	115.02(14)
Cu(1)–N(4)	2.088(3)	N(6)–Cu(1)–N(4)	108.42(13)
Cu(1)–N(1)	2.107(3)	C(16)–Cu(1)–N(1)	121.29(13)
Cu(2)–C(15)#1	1.885(4)	C(15)#1–Cu(2)–N(7)#2	119.78(14)
Cu(2)–N(7)#2	1.952(3)	N(5)–Cu(2)–N(2)	77.23(10)
Cu(2)–N(5)	2.082(3)	N(7)#2–Cu(2)–N(2)	102.21(11)
Cu(2)–N(2)	2.112(3)	C(15)#1–Cu(2)–N(2)	115.64(14)
N(6)–C(15)	1.150(5)	C(15)–N(6)–Cu(1)	176.5(3)
N(7)–C(16)	1.148(4)	N(7)–C(16)–Cu(1)	173.8(3)
Complex **2**			
Cu(1)–N(1)	2.090(3)	N(1)–Cu(1)–N(4)	78.2(3)
Cu(1)–N(4)	2.094(4)	C(15)#1–Cu(1)–N(6)	113.8(3)
Cu(1)–N(6)	1.965(4)	N(6)–Cu(1)–N(4)	119.5(3)
Cu(1)–C(15)#1	1.874(5)	C(15)#1–Cu(1)–N(1)	122.2(4)
N(6)–C(15)	1.148(5)	C(15)–N(6)–Cu(1)	166.0(9)
Cu(1)–Cu(1)#1	4.953(3)	N(6)–C(15)–Cu(1)#2	174.2(8)
Complex **3**			
Cu(1)–N(7)	1.930(13)	N(7)–Cu(1)–N(6)	148.2(5)
Cu(1)–N(6)	1.948(11)	N(7)–Cu(1)–N(5)#1	108.5(6)
Cu(1)–N(5)#1	2.158(12)	N(6)–Cu(1)–N(5)#1	102.6(5)
Cu(2)–C(15)	1.872(12)	C(15)–Cu(2)–N(1)	145.8(4)
Cu(2)–N(1)	2.052(11)	C(15)–Cu(2)–N(4)	132.5(4)
Cu(2)–N(4)	2.080(14)	N(1)–Cu(2)–N(4)	80.5(3)
Cu(2)···Cu(2)#2	3.046(12)	N(8)–Cu(3)–C(16)	131.6(7)
Cu(3)–N(8)	2.055(17)	N(8)–Cu(3)–C(16)#3	119.7(6)
Cu(3)–C(16)	2.072(14)	C(16)–Cu(3)–C(16)#3	107.6(6)
Cu(3)–C(16)#3	2.210(19)	C(16)–N(7)–Cu(1)	161.6(13)
Cu(3)···Cu(3)#3	2.532(16)	C(15)–N(6)–Cu(1)	162.3(8)
Complex **4**			
Cu(1)–C(15)#1	1.884(3)	N(1)–Cu(1)–N(4)	77.84(9)
Cu(1)–N(6)	1.994(3)	C(15)#1–Cu(1)–N(1)	119.76(11)
Cu(1)–N(1)	2.084(2)	C(15)#1–Cu(1)–N(6)	110.76(12)
Cu(1)–N(4)	2.099(2)	N(6)–Cu(1)–N(4)	101.90(11)

[a] Symmetry codes for **1**: #1 –*x* + 5/2, *y* – 1/2, –*z* + 3/2; #2 –*x* + 2, –*y*, –*z* + 2; **2**: #1 –*x*, *y* – 1/2, –*z* + 1/2; #2 –*x*, *y* + 1/2, –*z* + 1/2; **3**: #1 *x* – 1, *y*, *z* – 1; #2 –*x* + 1, –*y*, –*z*; #3 –*x*, –*y* + 1, –*z* – 1; **4**: #1 *x*, –*y* + 1/2, *z* – 1/2.

CCDC-635075 to -635078 contain the crystallographic data for for **1**–**4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): A schematic presentation of the 2D net in **1** (Figure S1), the 3D supramolecular structure of **1** projected along the *b*-axis (Figure S2), H-bond interactions in **2** (Figure S3), a schematic presentation of the staggered ladder chain in **3** (Figure S4), solid-state excitation and emission spectra of ligand L3 at room temperature (Figure S5), and XPRD patterns of **1**−**4** (Figure S6).

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