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A Series of Cu(II) Complexes Based on Different Bis(imidazole) Ligands and Organic Acids: Formation of Water Clusters and Fixation of Atmospheric Carbon Dioxide

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ABSTRACT: Two structurally related flexible bis(imidazole) ligands, 1,2-bis(imidazole-1-ylmethyl)-benzene (1,2-bix) and 1,4-bis(imidazole-1-ylmethyl)-benzene (1,4-bix), reacted with Cu(II) salts and various organic acids at room temperature, leading to the formation of nine novel metal-organic coordination architectures, from dinuclear structures to two-dimensional networks: $[\text{Cu}_2(\text{CO}_3)_2(1,2\text{-bix})_4] \cdot 8\text{H}_2\text{O}$ (**1**), $[\text{Cu}(\text{L}^1)(1,2\text{-bix})_2] \cdot 2\text{H}_2\text{O}$ (**2**), $[\text{Cu}_2(\text{L}^2)(1,2\text{-bix})_2(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$ (**3**), $[\text{Cu}(1,2\text{-bix})_2(\text{H}_2\text{O})_2] \cdot \text{L}^3 \cdot 4\text{H}_2\text{O}$ (**4**), $[\text{Cu}(\text{L}^4)_2][\text{Cu}(1,2\text{-bix})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**5**), $[\text{Cu}(\text{L}^5)(1,2\text{-bix})] \cdot \text{H}_2\text{O}$ (**6**), $[\text{Cu}_2(\text{L}^6)_2(1,2\text{-bix})_2] \cdot \text{H}_2\text{O}$ (**7**), $[\text{Cu}_2(\text{CO}_3)_2(1,4\text{-bix})_3] \cdot (1,4\text{-bix}) \cdot 10\text{H}_2\text{O}$ (**8**), and $[\text{Cu}(\text{L}^6)_2(1,4\text{-bix})][\text{Cu}(1,4\text{-bix})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (**9**) (H_2L^1 = 1,4-naphthalenedicarboxylic acid, H_4L^2 = 1,2,3,4-benzenetetracarboxylic acid, H_2L^3 = sebacic acid, H_2L^4 = maleic acid, H_2L^5 = fumaric acid, and H_2L^6 = 1,3-benzenedicarboxylic acid). All complexes were structurally characterized by X-ray diffraction analysis. The formation of water clusters and the fixation of atmospheric carbon dioxide in these complexes were observed. The organic anion effects on the structures of the complexes are also discussed.

Introduction

The rational design and synthesis of new discrete or polymeric metal-organic coordination architectures have received intense interest due to their fascinating structural topologies and potential applications as functional materials.¹ These coordination polymers can be specially designed by the careful selection of metal cations with preferred coordination geometries, the nature of the anions, the structure of the connecting ligands, and the reaction conditions.² Among those mentioned above, the selection of anions is extremely important because changing the structures of the anions can control and adjust the topologies of coordination frameworks, even for structures containing the same spacer ligand and metal cation.³ For example, it has been shown that the flexible bridging ligand 1,4-bis(imidazole-1-ylmethyl)-benzene (1,4-bix) gives an infinite two-dimensional (2D) polyrotaxane network if reacted with Cd(II) sulfate hexahydrate;⁴ however, a triply interpenetrating α -polonium topology is produced if reacted with Cd(II) nitrate hexahydrate.⁵ In our previous studies, the flexible bridging ligand 1,1'-(1,4-butanediyl)bis(imidazole) formed the rare three-dimensional (3D) four-connected 8⁶ net after reaction with Cu(II) and 1,3-benzenedicarboxylic acid,^{3f} and a 3D 2-fold interpenetrating 4⁶6⁴ net through reaction with Cu(II) and 1,1'-ferrocenedicarboxylic acid.^{3g} It is clear that the structures of the anions play an important role in the formation of these architectures. So far, although the effect of anions on the structures of complexes has been studied, systematic investigations on the influence of organic anions such as polycarboxylate ligands on their complex structures have been lacking.³

In order to investigate the effect of the organic ligands, particularly the organic anions, on their complex structures, we selected six structurally different organic acids as the anions and two flexible bis(imidazole) ligands as the secondary ligands

(Scheme 1). Nine new Cu(II) complexes with different structures, $[\text{Cu}_2(\text{CO}_3)_2(1,2\text{-bix})_4] \cdot 8\text{H}_2\text{O}$ (**1**), $[\text{Cu}(\text{L}^1)(1,2\text{-bix})_2] \cdot 2\text{H}_2\text{O}$ (**2**), $[\text{Cu}_2(\text{L}^2)(1,2\text{-bix})_2(\text{H}_2\text{O})_4] \cdot 8\text{H}_2\text{O}$ (**3**), $[\text{Cu}(1,2\text{-bix})_2(\text{H}_2\text{O})_2] \cdot \text{L}^3 \cdot 4\text{H}_2\text{O}$ (**4**), $[\text{Cu}(\text{L}^4)_2][\text{Cu}(1,2\text{-bix})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**5**), $[\text{Cu}(\text{L}^5)(1,2\text{-bix})] \cdot \text{H}_2\text{O}$ (**6**), $[\text{Cu}_2(\text{L}^6)_2(1,2\text{-bix})_2] \cdot \text{H}_2\text{O}$ (**7**), $[\text{Cu}_2(\text{CO}_3)_2(1,4\text{-bix})_3] \cdot (1,4\text{-bix}) \cdot 10\text{H}_2\text{O}$ (**8**), and $[\text{Cu}(\text{L}^6)_2(1,4\text{-bix})][\text{Cu}(1,4\text{-bix})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (**9**), where 1,2-bix = 1,2-bis(imidazol-1-ylmethyl)benzene, 1,4-bix = 1,4-bis(imidazol-1-ylmethyl)benzene, H_2L^1 = 1,4-naphthalenedicarboxylic acid, H_4L^2 = 1,2,3,4-benzenetetracarboxylic acid, H_2L^3 = sebacic acid, H_2L^4 = maleic acid, H_2L^5 = fumaric acid, and H_2L^6 = 1,3-benzenedicarboxylic acid, were obtained by varying the organic acids. The formation of water clusters and the fixation of atmospheric carbon dioxide were observed in the complexes. The organic anion effects on the structures of the complexes were also discussed.

Experimental Section

Materials and Methods. All reagents and solvents for syntheses were purchased from commercial sources and used as received. A Perkin-Elmer 240 elemental analyzer was used to collect microanalytical data. The X-ray powder diffraction (XRPD) data were collected on a Siemens D5005 diffractometer with Cu K α radiation (λ = 1.5418 Å), and the recording speed was 0.3°/min over the 2θ range of 4–30° at room temperature. The simulated and experimental XRPD patterns of the compounds **1–9** are shown in the Supporting Information (Figures S1–S9). The experimental patterns are in good agreement with the corresponding simulated ones, indicating phase purity of the synthesized products.

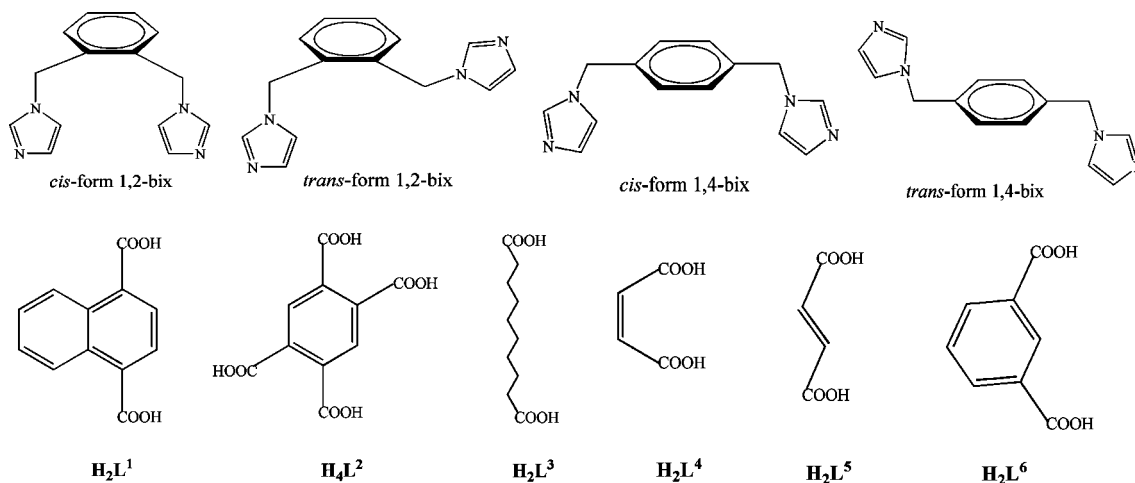
Syntheses of 1,2-bix and 1,4-bix. The two bis(imidazole) ligands were prepared as previously described.⁶ A solution containing imidazole (3.16 g, 46.4 mmol) and α,α' -dibromo-*o*-xylene or α,α' -dibromo-*p*-xylene (1.18 g, 4.46 mmol) in methanol (45 mL) was heated under reflux for 10 h. Removal of most of the solvent at reduced pressure gave a light yellow syrup which was dissolved in 100 mL of aqueous K_2CO_3 (6.13 g). This solution, upon standing, yielded crystalline of 1,2-bix or 1,4-bix, which was recrystallized from water. Calc. for $\text{C}_{14}\text{H}_{14}\text{N}_4$: C, 70.59; H, 5.88, N, 23.53. Found: C, 70.78; H, 5.62; N, 23.33.

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Scheme 1. The Organic Acid Ligands Used in the Construction of Cu(II) Compounds

Table 1. Crystallographic Data for Compounds 1–5^a

compound	1	2	3	4	5
formula	C ₅₈ H ₇₂ Cu ₂ N ₁₆ O ₁₄	C ₄₀ H ₃₄ CuN ₈ O ₆	C ₁₉ H ₂₇ CuN ₄ O ₁₀	C ₃₈ H ₅₆ CuN ₈ O ₁₀	C ₃₆ H ₄₂ Cu ₂ N ₈ O ₁₃
formula mass	1344.40	786.29	534.99	848.45	921.86
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	8.873(6)	8.6238(17)	13.915(3)	8.5953(17)	8.6728(17)
<i>b</i> [Å]	9.049(4)	9.5937(19)	9.6531(19)	9.2493(18)	8.7479(17)
<i>c</i> [Å]	19.178(10)	12.022(2)	17.322(4)	13.537(3)	13.418(3)
α [deg]	90.04(4)	110.52(3)	90	93.47(3)	91.98(3)
β [deg]	96.74(4)	103.40(3)	96.56(3)	103.54(3)	93.34(3)
γ [deg]	94.99(4)	91.34(3)	90	95.16(3)	98.97(3)
<i>V</i> [Å ³]	1523.3(15)	900.1(3)	2311.6(8)	1038.4(4)	1002.9(3)
<i>Z</i>	1	1	4	1	1
ρ [g cm ⁻³]	1.466	1.451	1.537	1.357	1.526
μ [mm ⁻¹]	0.777	0.668	1.007	0.591	1.135
goodness-of-fit on <i>F</i> ²	1.006	1.185	0.773	0.927	0.908
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0382 <i>wR</i> ₂ = 0.0890	<i>R</i> ₁ = 0.0544 <i>wR</i> ₂ = 0.1684	<i>R</i> ₁ = 0.0465 <i>wR</i> ₂ = 0.1078	<i>R</i> ₁ = 0.0516 <i>wR</i> ₂ = 0.1467	<i>R</i> ₁ = 0.0456 <i>wR</i> ₂ = 0.1068

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

Table 2. Crystallographic Data for Compounds 6–9^a

compound	6	7	8	9
formula	C ₁₈ H ₁₈ CuN ₄ O ₅	C ₂₂ H ₁₉ CuN ₄ O _{4.50}	C ₂₉ H ₃₈ CuN ₈ O ₈	C ₅₈ H ₆₂ Cu ₂ N ₁₂ O ₁₄
formula mass	433.90	474.95	690.21	1278.28
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	9.0079(18)	10.081(2)	12.245(2)	8.6401(17)
<i>b</i> [Å]	15.629(3)	15.983(3)	12.559(3)	13.569(3)
<i>c</i> [Å]	14.264(3)	13.270(3)	12.983(3)	13.734(3)
α [deg]	90	90	103.75(3)	82.65(3)
β [deg]	106.02(3)	108.60(3)	98.64(3)	71.95(3)
γ [deg]	90	90	118.67(3)	89.35(3)
<i>V</i> [Å ³]	1930.2(7)	2026.5(7)	1617.9(6)	1517.7(5)
<i>Z</i>	4	4	2	1
ρ [g cm ⁻³]	1.493	1.557	1.417	1.399
μ [mm ⁻¹]	1.169	1.119	0.736	0.775
goodness-of-fit on <i>F</i> ²	0.780	0.898	0.844	0.908
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0692 <i>wR</i> ₂ = 0.1487	<i>R</i> ₁ = 0.0335 <i>wR</i> ₂ = 0.0451	<i>R</i> ₁ = 0.0500 <i>wR</i> ₂ = 0.1058	<i>R</i> ₁ = 0.0701 <i>wR</i> ₂ = 0.1579

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

Synthesis of [Cu₂(CO₃)₂(1,2-bix)₄]·8H₂O (1). After a mixture of CuCl₂·2H₂O (0.171 g, 1 mmol) and NaOH (0.080 g, 2 mmol) in water (10 mL) was stirred for 10 min, the Cu(OH)₂ was collected, and washed with water. The Cu(OH)₂ (1 mmol) and 1,2-bix (0.238 g, 1 mmol) were then dissolved in a minimum amount of ammonia (14 M, 15 mL). Suitable blue crystals of **1** were obtained by slow evaporation of the ammoniacal solution at ambient temperature in 37% yield. Calc. for C₅₈H₇₂Cu₂N₁₆O₁₄: C, 51.77; H, 5.36; N, 16.66%. Found: C, 51.61; H, 5.50; N, 16.47%. IR data (KBr, cm⁻¹): 3396m, 3099w, 1647w, 1566s, 1518s, 1463w, 1299m, 1243m, 1090m, 844w, 743m, 658m, 620w.

Synthesis of [Cu(L¹)(1,2-bix)₂]·2H₂O (2). A mixture of CuCl₂·2H₂O (0.171 g, 1 mmol), NaOH (0.080 g, 2 mmol) and H₂L¹

(0.216 g, 1 mmol) in water was stirred for 10 min at 60 °C, then 1,2-bix (0.238 g, 1 mmol) was added to the mixture. After the mixture was stirred for 30 min, blue precipitate was collected, and dissolved in a minimum amount of ammonia (14 M). Suitable blue crystals of **2** were obtained by slow evaporation of the ammonia solution at ambient temperature in 41% yield. Calc. for C₄₀H₃₄CuN₈O₆: C, 61.05; H, 4.32; N, 14.24%. Found: C, 60.87; H, 4.51; N, 14.39%. IR data (KBr, cm⁻¹): 3465m, 3134w, 1643w, 1561s, 1516s, 1461w, 1401m, 1358s, 1235w, 1111m, 1087w, 1027w, 946w, 849w, 790m, 743m, 662m, 588w.

Synthesis of [Cu₂(L²)(1,2-bix)₂(H₂O)₄]·8H₂O (3). Compound **3** was prepared in 53% yield in the same way as for **2**, using H₄L² instead of H₂L¹. Calc. for C₁₉H₂₇CuN₄O₁₀: C, 42.62; H, 5.05; N, 10.47%. Found:

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 1–9^a

Complex 1			
Cu(1)–O(1)	1.9772(16)	Cu(1)–O(3)	1.9958(16)
Cu(1)–N(1)	1.9651(19)	Cu(1)–N(4)	1.9999(18)
Cu(1)–N(8) ^{#1}	2.258(2)	N(1)–Cu(1)–O(3)	95.78(7)
N(1)–Cu(1)–O(1)	161.17(6)	O(1)–Cu(1)–O(3)	66.15(7)
N(1)–Cu(1)–N(4)	97.93(8)	O(1)–Cu(1)–N(4)	97.24(7)
O(3)–Cu(1)–N(4)	155.21(6)	N(1)–Cu(1)–N(8) ^{#1}	96.59(8)
O(1)–Cu(1)–N(8) ^{#1}	93.49(7)	O(3)–Cu(1)–N(8) ^{#1}	105.13(7)
N(4)–Cu(1)–N(8) ^{#1}	93.71(8)	Complex 2	
Cu(1)–N(1)	2.002(3)	Cu(1)–N(4) ^{#3}	2.002(3)
N(4) ^{#2} –Cu(1)–N(1)	90.34(12)	N(1) ^{#4} –Cu(1)–N(1)	180
N(4) ^{#3} –Cu(1)–N(1)	89.66(12)	N(4) ^{#3} –Cu(1)–N(4) ^{#4}	180
Complex 3			
Cu(1)–O(2W)	1.981(5)	Cu(1)–N(3)	2.016(4)
Cu(1)–N(1)	2.018(4)	Cu(1)–O(1)	2.027(3)
Cu(1)–O(1W)	2.339(4)	O(2W)–Cu(1)–N(3)	177.44(19)
N(1)–Cu(1)–O(1W)	113.35(16)	O(2W)–Cu(1)–N(1)	88.83(18)
N(3)–Cu(1)–N(1)	88.62(17)	O(2W)–Cu(1)–O(1)	89.61(17)
N(3)–Cu(1)–O(1)	92.88(15)	N(1)–Cu(1)–O(1)	161.89(16)
O(2W)–Cu(1)–O(1W)	92.24(17)	N(3)–Cu(1)–O(1W)	88.56(16)
O(1)–Cu(1)–O(1W)	84.73(14)	Complex 4	
Cu(1)–N(2)	2.016(2)	Cu(1)–N(3) ^{#2}	2.008(2)
N(3) ^{#2} –Cu(1)–N(3) ^{#3}	180	N(3) ^{#2} –Cu(1)–N(2)	89.03(9)
N(3) ^{#3} –Cu(1)–N(2)	90.97(9)	N(2) ^{#4} –Cu(1)–N(2)	180
Complex 5			
Cu(1)–N(1)	1.997(3)	Cu(2)–O(1)	1.913(3)
Cu(2)–O(3)	1.935(3)	Cu(1)–N(4) ^{#5}	2.034(3)
N(1)–Cu(1)–N(1) ^{#1}	180	N(1)–Cu(1)–N(4) ^{#2}	90.59(11)
N(1)–Cu(1)–N(4) ^{#2}	89.41(11)	N(4) ^{#5} –Cu(1)–N(4) ^{#2}	180
O(1)–Cu(2)–O(3)	90.89(13)	O(1)–Cu(2)–O(3) ^{#6}	89.11(13)
O(1) ^{#6} –Cu(2)–O(1)	180	O(3)–Cu(2)–O(3) ^{#6}	180
Complex 6			
Cu(1)–N(3)	1.965(7)	Cu(1)–O(1)	1.981(4)
Cu(1)–N(1) ^{#7}	1.964(7)	Cu(1)–O(3) ^{#8}	1.999(4)
N(1) ^{#7} –Cu(1)–N(3)	178.2(3)	N(1) ^{#7} –Cu(1)–O(1)	91.3(3)
N(3)–Cu(1)–O(1)	87.0(3)	N(1) ^{#7} –Cu(1)–O(3) ^{#9}	89.4(3)
N(3)–Cu(1)–O(3) ^{#9}	92.3(3)	O(1)–Cu(1)–O(3) ^{#9}	176.0(2)
Complex 7			
Cu(1)–O(1)	1.9608(13)	Cu(1)–N(4) ^{#10}	1.9674(17)
Cu(1)–O(2) ^{#10}	2.3347(15)	Cu(1)–O(3) ^{#10}	2.0434(13)
O(1)–Cu(1)–N(4) ^{#10}	89.36(6)	O(1)–Cu(1)–N(1)	90.67(6)
N(4) ^{#10} –Cu(1)–N(1)	174.17(8)	O(1)–Cu(1)–O(3) ^{#8}	144.73(6)
N(4) ^{#10} –Cu(1)–O(3) ^{#8}	90.69(7)	N(1)–Cu(1)–O(3) ^{#8}	92.65(7)
O(1)–Cu(1)–O(2) ^{#10}	131.57(6)	N(4) ^{#10} –Cu(1)–O(2) ^{#10}	86.88(6)
N(1)–Cu(1)–O(2) ^{#10}	88.74(7)	O(3) ^{#8} –Cu(1)–O(2) ^{#10}	83.63(6)
Complex 8			
Cu(1)–N(1)	1.967(2)	Cu(1)–O(1)	1.994(2)
Cu(1)–N(5)	2.047(3)	Cu(1)–O(2)	1.964(2)
Cu(1)–N(4) ^{#11}	2.149(3)	O(2)–Cu(1)–O(1)	65.83(10)
O(2)–Cu(1)–N(1)	163.66(10)	O(2)–Cu(1)–N(5)	94.91(11)
N(1)–Cu(1)–O(1)	98.12(10)	O(1)–Cu(1)–N(5)	141.07(12)
N(1)–Cu(1)–N(5)	96.33(10)	N(1)–Cu(1)–N(4) ^{#12}	95.17(11)
O(2)–Cu(1)–N(4) ^{#12}	94.34(11)	N(5)–Cu(1)–N(4) ^{#12}	100.71(10)
O(1)–Cu(1)–N(4) ^{#12}	113.67(11)	Complex 9	
Cu(1)–N(3)	2.002(3)	Cu(1)–N(1)	2.007(4)
Cu(2)–N(5)	1.967(6)	Cu(2)–O(1)	1.955(4)
N(3)–Cu(1)–N(3) ^{#6}	180	N(3)–Cu(1)–N(1) ^{#6}	92.16(14)
N(3)–Cu(1)–N(1)	87.84(14)	O(1) ^{#13} –Cu(2)–N(5)	88.3(2)
N(1) ^{#6} –Cu(1)–N(1)	180	O(1)–Cu(2)–N(5)	91.7(2)
N(5)–Cu(2)–N(5) ^{#13}	180	O(1) ^{#13} –Cu(2)–O(1)	180

^a Symmetry transformations used to generate equivalent atoms: ^{#1} $-x + 1, -y + 1, -z + 2$; ^{#2} $x, y - 1, z$; ^{#3} $-x + 2, -y + 1, -z + 1$; ^{#4} $-x + 2, -y, -z + 1$; ^{#5} $-x + 1, -y + 2, -z + 2$; ^{#6} $-x, -y + 2, -z + 2$; ^{#7} $-x + 1, -y + 1, -z$; ^{#8} $x - 1, y, z$; ^{#9} $x + 1, y, z$; ^{#10} $-x + 1, -y, -z + 1$; ^{#11} $x - 1, y - 1, z$; ^{#12} $x + 1, y + 1, z$; ^{#13} $-x, -y + 3, -z + 1$.

C, 42.43; H, 5.33; N, 10.61%. IR data (KBr, cm^{-1}): 3422m, 3124w, 1676w, 1645m, 1605s, 1561s, 1519m, 1429w, 1356s, 1239w, 1101m, 1028w, 949w, 851w, 749m, 715w, 660m.

Synthesis of $[\text{Cu}(\text{L}^3\text{-bix})_2(\text{H}_2\text{O})_2] \cdot \text{L}^3 \cdot 4\text{H}_2\text{O}$ (4). Compound 4 was prepared in 47% yield in the same way as for 2, using H_2L^3 instead of H_2L^1 . Calc. for $\text{C}_{38}\text{H}_{56}\text{CuN}_8\text{O}_{10}$: C, 53.75; H, 6.60; N, 13.20%. Found: C, 53.56; H, 6.53; N, 13.42%. IR data (KBr, cm^{-1}): 3744m, 3423m, 3120w, 1740w, 1698m, 1645m, 1549s, 1516s, 1455w, 1394m, 1234w, 1105w, 950w, 835w, 752w, 659m, 524w.

Synthesis of $[\text{Cu}(\text{L}^4)_2][\text{Cu}(\text{L}^4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (5). Compound 5 was prepared in 49% yield in the same way as for 2, using H_2L^4 instead of H_2L^1 . Calc. for $\text{C}_{36}\text{H}_{42}\text{Cu}_2\text{N}_8\text{O}_{13}$: C, 46.86; H, 4.56; N, 12.15%. Found: C, 46.71; H, 4.50; N, 12.28%. IR data (KBr, cm^{-1}):

3424m, 3121w, 1671w, 1642m, 1603s, 1566s, 1520s, 1359s, 1244w, 1114m, 1001w, 832w, 799w, 783m, 687m.

Synthesis of $[\text{Cu}(\text{L}^5)(1,2\text{-bix})_2] \cdot \text{H}_2\text{O}$ (6). Compound 6 was prepared in 55% yield in the same way as for 2, using H_2L^5 instead of H_2L^1 . Calc. for $\text{C}_{18}\text{H}_{18}\text{CuN}_4\text{O}_5$: C, 49.78; H, 4.15; N, 12.91%. Found: C, 49.67; H, 4.19; N, 12.76%. IR data (KBr, cm^{-1}): 3423m, 3123w, 1676w, 1645m, 1604s, 1565s, 1524s, 1455w, 1356s, 1236w, 1112m, 999w, 955w, 831w, 793w, 781m, 684m, 652w.

Synthesis of $[\text{Cu}_2(\text{L}^6)_2(1,2\text{-bix})_2] \cdot \text{H}_2\text{O}$ (7). Compound 7 was prepared in 44% yield in the same way as for 2, using H_2L^6 instead of H_2L^1 . Calc. for $\text{C}_{22}\text{H}_{19}\text{Cu}_2\text{N}_4\text{O}_{4.5}$: C, 55.58; H, 4.00; N, 11.79%. Found: C, 55.44; H, 4.13; N, 11.64%. IR data (KBr, cm^{-1}): 3425m, 3133w,

Table 4. Hydrogen Bonds for 1–2, 4–5, and 7–8 [Å and deg]^a

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
Complex 1				
O(1W)–HW11···O(3)	0.868(16)	1.901(17)	2.768(3)	177(3)
O(1W)–HW12···O(4W) ^{#1}	0.939(16)	2.03(3)	2.750(3)	132(2)
O(2W)–HW21···O(1)	0.893(18)	1.937(19)	2.813(3)	166(3)
O(2W)–HW22···O(1W) ^{#2}	0.883(18)	1.890(19)	2.756(3)	166(3)
O(3W)–HW31···O(2)	0.879(17)	1.927(17)	2.804(3)	175(3)
O(3W)–HW32···O(2W)	0.909(17)	2.04(2)	2.891(3)	155(3)
O(4W)–HW41···O(2) ^{#1}	0.896(17)	2.04(2)	2.814(3)	144(2)
O(4W)–HW42···N(7)	0.886(17)	1.916(18)	2.797(3)	173(3)
Complex 2				
O(1W)–HW12···O(2)	0.858(19)	2.00(2)	2.855(6)	173(5)
O(1W)–HW11···O(2) ^{#3}	0.85(2)	2.02(3)	2.858(5)	165(7)
Complex 4				
O(1W)–HW12···O(1)	0.834(19)	2.03(2)	2.864(3)	174(5)
O(1W)–HW11···O(1) ^{#5}	0.831(19)	2.06(2)	2.862(4)	163(4)
O(2W)–HW22···O(3W) ^{#4}	0.869(19)	1.98(3)	2.794(4)	156(5)
O(2W)–HW21···O(1)	0.86(2)	2.09(3)	2.910(4)	159(6)
O(3W)–HW31···O(2) ^{#6}	0.841(19)	1.94(2)	2.783(4)	177(5)
O(3W)–HW32···O(2)	0.840(19)	1.96(2)	2.797(4)	173(4)
Complex 5				
O(1W)–HW12···O(3) ^{#4}	0.839(18)	2.11(2)	2.919(4)	162(4)
O(1W)–HW11···O(2)	0.841(18)	1.96(2)	2.777(4)	165(4)
O(2W)–HW21···O(2)	0.853(19)	2.03(5)	2.781(5)	146(8)
O(2W)–HW22···O(4) ^{#4}	0.84(2)	1.99(2)	2.822(5)	174(7)
O(3W)–HW31···O(2W) ^{#7}	0.86(2)	1.98(6)	2.802(10)	161(16)
Complex 7				
O(1W)–HW11···O(3) ^{#1}	0.89(2)	2.18(3)	2.998(4)	153(4)
O(1W)–HW12···O(3) ^{#8}	0.915(17)	2.21(4)	2.994(4)	143(5)
Complex 8				
O(1W)–HW11···O(3)	0.88(2)	1.90(2)	2.782(4)	172(6)
O(1W)–HW12···O(2W) ^{#9}	0.89(2)	2.16(2)	3.035(5)	170(5)
O(2W)–HW21···O(1W) ^{#10}	0.931(19)	1.91(2)	2.822(5)	168(4)
O(2W)–HW22···O(5W) ^{#1}	0.912(19)	1.93(2)	2.815(5)	164(4)
O(3W)–HW32···O(1)	0.864(19)	2.10(3)	2.722(4)	128(3)
O(3W)–HW31···O(5W)	0.854(19)	2.261(19)	2.808(5)	122(2)
O(4W)–HW41···O(3)	0.837(19)	1.95(3)	2.687(4)	146(5)
O(4W)–HW42···O(3W)	0.927(16)	2.47(3)	3.079(6)	123(2)
O(5W)–HW52···N(8) ^{#11}	0.837(19)	2.21(3)	2.886(6)	138(4)
O(5W)–HW51···O(4W) ^{#12}	0.933(16)	2.18(3)	2.817(5)	125(3)

^a Symmetry transformations used to generate equivalent atoms: ^{#1} $-x + 1, -y, -z + 1$; ^{#2} $x + 1, y, z$; ^{#3} $-x + 2, -y + 1, -z + 2$; ^{#4} $x, y - 1, z$; ^{#5} $-x + 3, -y, -z + 1$; ^{#6} $-x + 3, -y + 1, -z + 1$; ^{#7} $-x + 1, -y + 1, -z + 3$; ^{#8} $x - 1, y, z$; ^{#9} $x, y, z - 1$; ^{#10} $-x + 1, -y + 1, -z + 1$; ^{#11} $x, y - 1, z - 1$; ^{#12} $-x + 1, -y, -z$.

1628m, 1607s, 1560m, 1523m, 1361s, 1233w, 1114m, 950w, 836w, 746s, 711sw, 651m, 529w.

Synthesis of $[\text{Cu}_2(\text{CO}_3)_2(1,4\text{-bix})_3] \cdot (1,4\text{-bix}) \cdot 10\text{H}_2\text{O}$ (8). Compound **8** was prepared in 39% yield in the same way as for **1**, using 1,4-bix instead of 1,2-bix. Calc. for $\text{C}_{29}\text{H}_{38}\text{Cu}_2\text{N}_8\text{O}_8$: C, 50.42; H, 5.51; N, 16.23%. Found: C, 50.26; H, 5.32; N, 16.53%. IR data (KBr, cm^{-1}): 3394m, 3097w, 1645w, 1564s, 1516s, 1447w, 1298m, 1241m, 1091m, 1029w, 934w, 843w, 743m, 659m, 622w, 514w.

Synthesis of $[\text{Cu}(\text{L}^6)_2(1,4\text{-bix})][\text{Cu}(1,4\text{-bix})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ (9). Compound **9** was prepared in 38% yield in the same way as for **7**, using 1,4-bix instead of 1,2-bix. Calc. for $\text{C}_{58}\text{H}_{62}\text{Cu}_2\text{N}_{12}\text{O}_{14}$: C, 54.45; H, 4.85; N, 13.14%. Found: C, 54.25; H, 4.63; N, 13.27%. IR data (KBr, cm^{-1}): 3743m, 3422m, 3122w, 1740w, 1693m, 1645m, 1614m, 1560s, 1516s, 1465w, 1366m, 1239w, 1096m, 949w, 841w, 745w, 661w.

X-ray Crystallography. Single-crystal X-ray diffraction data for complex **1** was recorded on a Bruker-AXS Smart CCD diffractometer, using ω scan technique with Mo K α radiation ($\lambda = 0.71073$ Å). Crystallographic data for compounds **2–9** were collected on a Rigaku RAXIS-RAPID single crystal diffractometer equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo–K α radiation, $\lambda = 0.71073$ Å) at a temperature of 20 ± 2 °C. The data processing was accomplished with the PROCESS-AUTO processing program. The structures of the compounds were solved by

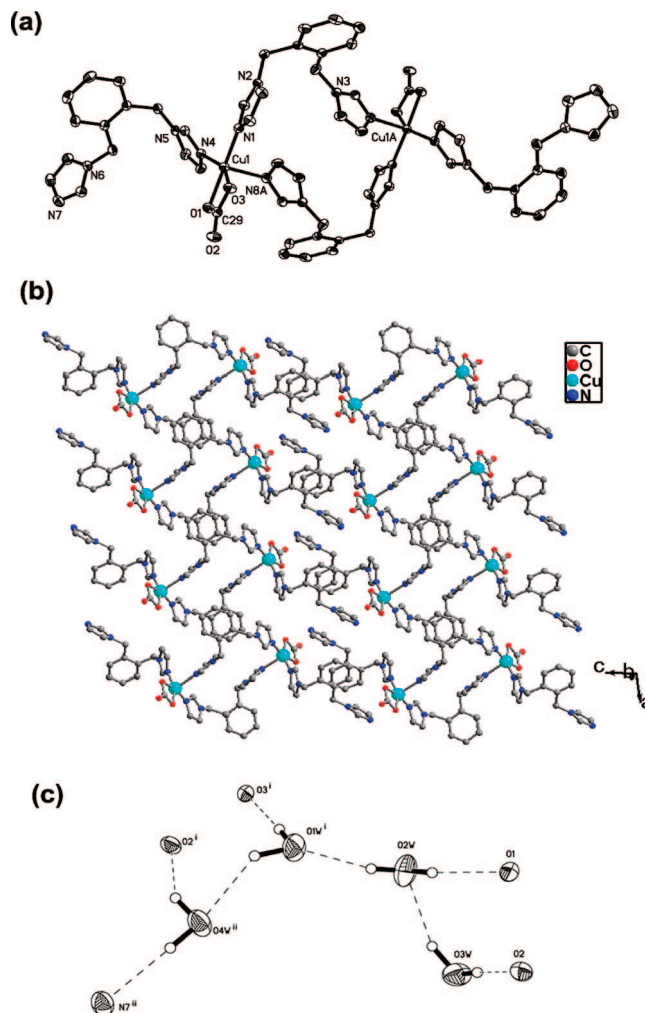


Figure 1. Views of (a) the dinuclear compound **1**, (b) the 2D supramolecular structure of **1** formed through π – π interactions, and (c) the acyclic water tetramer and its coordination environment (symmetry code: (i) $1 + x, y, z$; (ii) $2 - x, -y, 1 - z$).

direct method using the program SHELXS-97⁷ and refined by full-matrix least-squares techniques against F^2 using the SHELXL-97⁸ crystallographic software package. All non-hydrogen atoms were easily found from the Fourier difference maps and refined anisotropically, whereas the hydrogen atoms of the organic molecules were placed by geometrical considerations and were added to the structure factor calculation. The hydrogen atoms of water molecules for **1–2**, **4–5**, and **7–8** were located from Fourier difference maps. The detailed crystallographic data and structure refinement parameters for **1–9** are summarized in Tables 1 and 2.

Results and Discussion

Preparation of Complexes 1–9. Both ligands 1,2-bix and 1,4-bix are very soluble in common polar organic solvents such as CH_3OH and CH_3CN . Their complexes **1–9** were obtained as crystalline compounds in water by combination of the corresponding neutral ligand (bix) with Cu(II) polycarboxylate salts at room temperature. Complexes **1**, **2**, **4** and **8** have the same Cu(II):bix composition of 1:2. For complexes **3** and **5–7**, a Cu(II):bix ratio of 1:1 was achieved, whereas compound **9** has a Cu(II):bix ratio of 2:3. Although we varied the Cu(II):bix ratio (1:1, 1:1.5, 1:2, 1.5:1, and 2:1) in the reaction mixtures, the same compounds **1–9** were obtained, respectively, indicating that the complex structures obtained by this reaction are not sensitive to the Cu(II):bix ratios. However, although the products

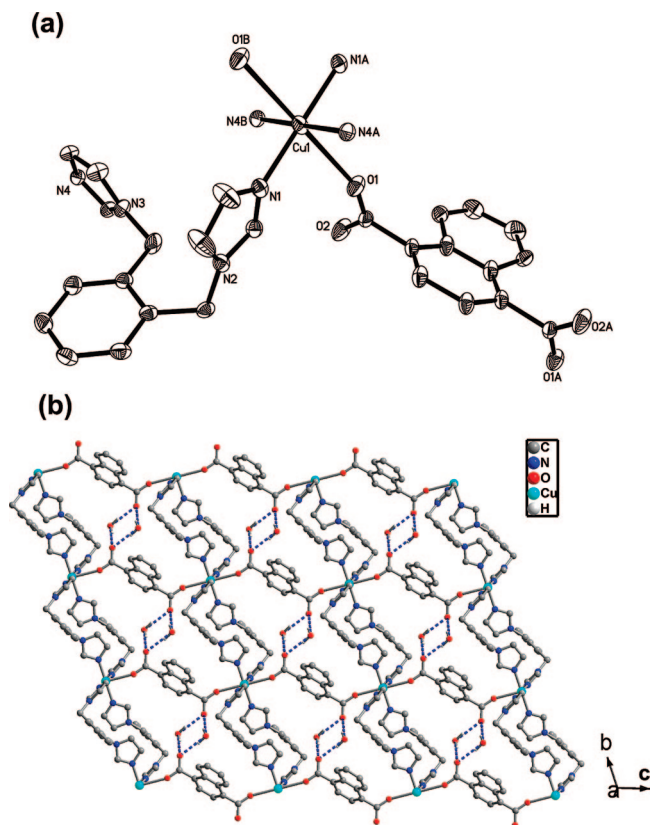


Figure 2. (a) The coordination environment of Cu(II) center in compound **2**, and (b) the 2D network structure of **2**.

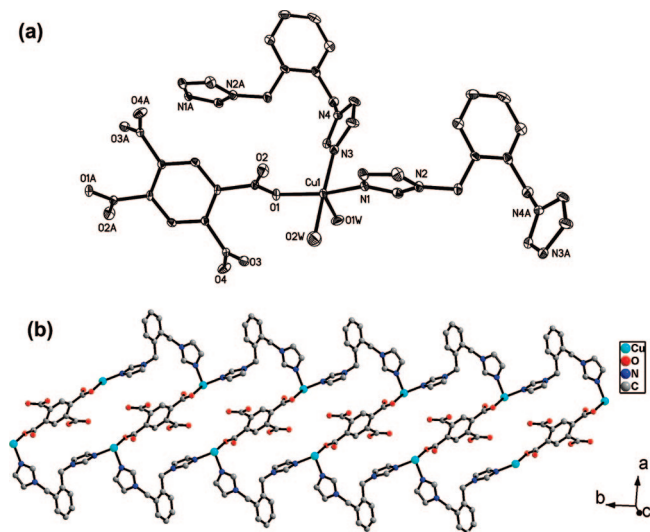


Figure 3. (a) The coordination environment of Cu(II) center in compound **3**, and (b) the 1D ladder structure of **3**.

1–9 do not depend on this ratio, increasing the bix:Cu(II) ratio resulted in somewhat higher yields and better crystal quality. Compounds **1–9** are air stable and retain their structural integrity at room temperature.

Description of Crystal Structures. Selected bond distances and angles for compounds **1–9** are listed in Table 3. Hydrogen-bond parameters for **1–2**, **4–5**, and **7–8** are shown in Table 4. Single-crystal X-ray structural analysis shows that compound **1**, $[\text{Cu}_2(\text{CO}_3)_2(1,2\text{-bix})_4] \cdot 8\text{H}_2\text{O}$, is a dinuclear complex (Figure 1a) with two pendant arms. The central Cu(II) cation adopts a distorted square-pyramidal geometry by coordinating to three

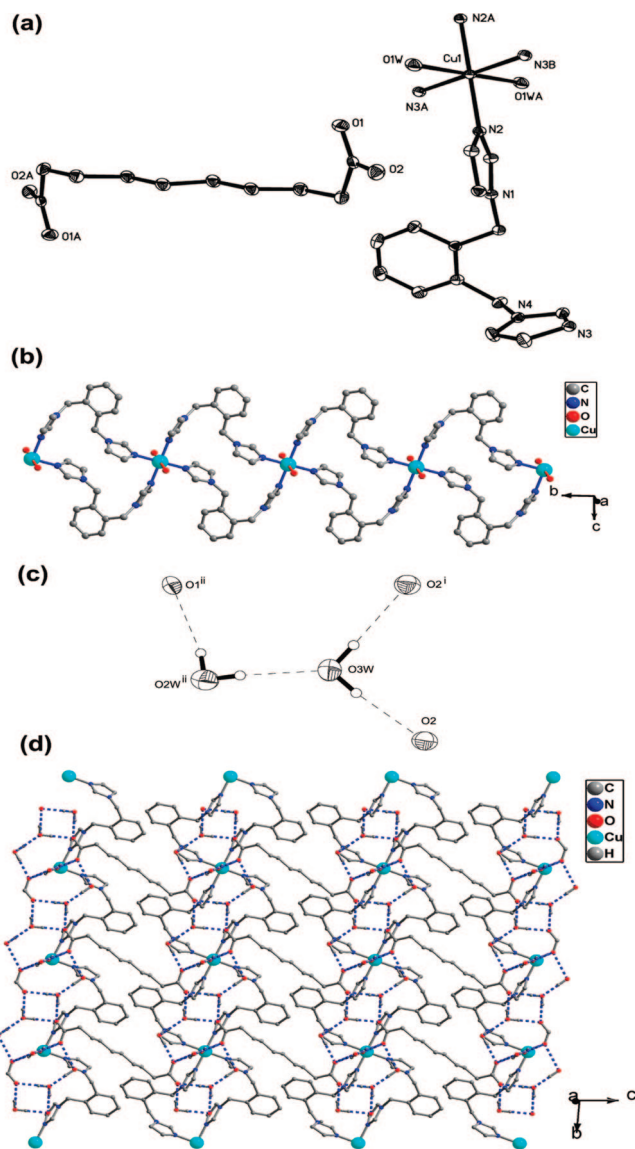


Figure 4. (a) The coordination environment of the Cu(II) center in compound **4**, (b) the 1D chain structure of **4**, (c) the water dimer in **4** (symmetry codes: (i) $3 - x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$), and (d) the 3D hydrogen-bonding structure of **4**.

nitrogen atoms from three distinct 1,2-bix ligands, and two oxygen atoms from one CO_3^{2-} anion. Two nitrogen atoms (N1 and N4) and two oxygen atoms (O1 and O3) constitute the base of the square-pyramid, whereas one nitrogen atom (N8A) occupies the apical position with a Cu–N8A distance of 2.258(2) Å. Interestingly, the 1,2-bix ligands exhibit two types of coordination modes: one acts as a bidentate bridging ligand, while the other shows monodentate coordination. This observation is entirely different from the situation in most bis(imidazole) complexes, in which the bis(imidazole) ligands usually connect the metal cations in the bidentate bridging mode.⁹ It is also noteworthy that the flexible 1,2-bix ligand shows the *trans* conformation with a Cu(II)···Cu(II) separation of 9.55 Å. In addition, there are two types of π – π interactions between the neighboring dimers: one is between benzene rings (centroid-to-centroid distance of 3.71 Å, vertical face-to-face distance of 3.41 Å, and dihedral angle of 0.28°), while the other is between imidazole rings (centroid-to-centroid distance of 3.88 Å, vertical face-to-face distance of 3.31 Å, and dihedral angle of 0.44°). This results in 2D networks (Figure 1b).

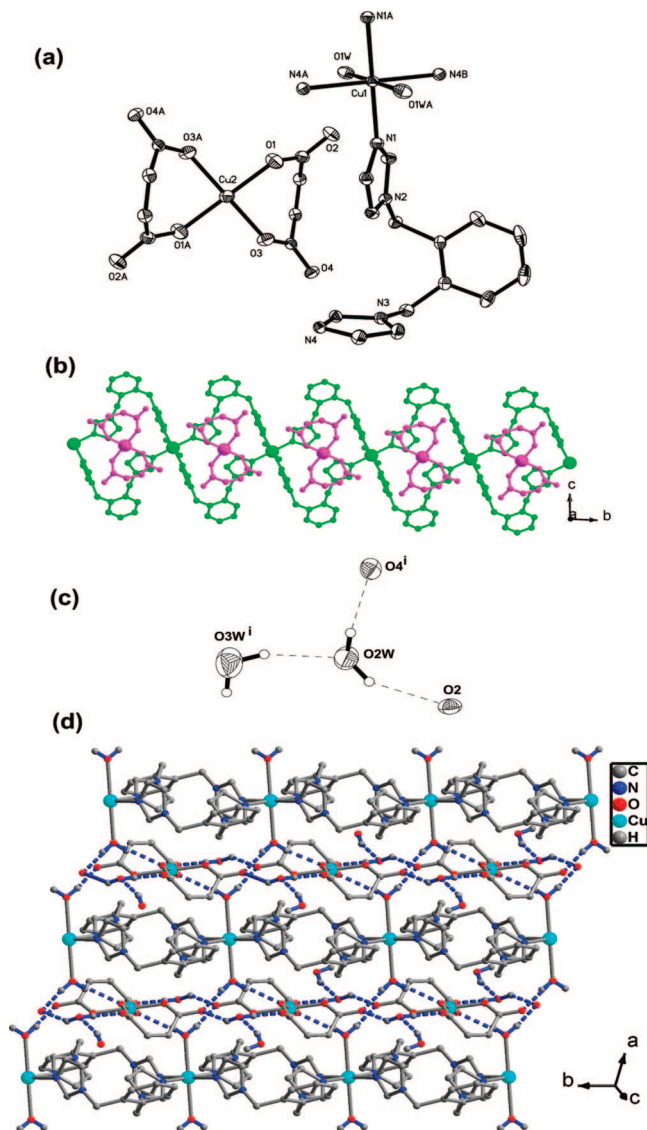


Figure 5. (a) The coordination environment of the Cu(II) center in compound 5, (b) the 1D chain and discrete monomer substructures in 5, (c) the water dimer in 5 (symmetry codes: (i) $1-x, 1-y, 3-z$; (ii) $x, y-1, z$), and (d) the 3D hydrogen-bonding structure of 5.

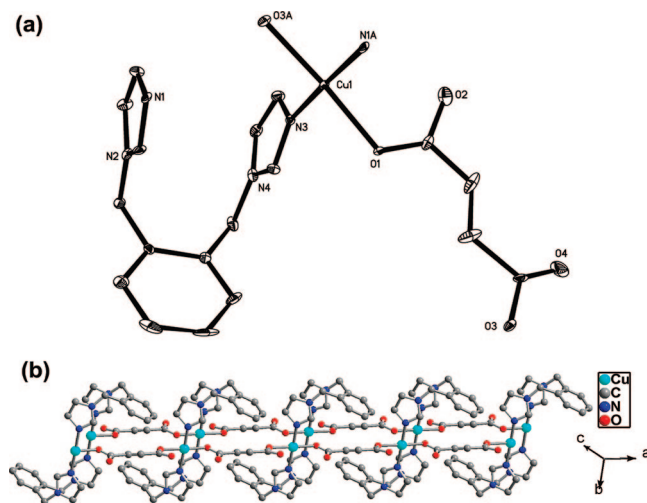


Figure 6. (a) The coordination environment of the Cu(II) center in compound 6, and (b) the 1D looplike ladder structure of 6.

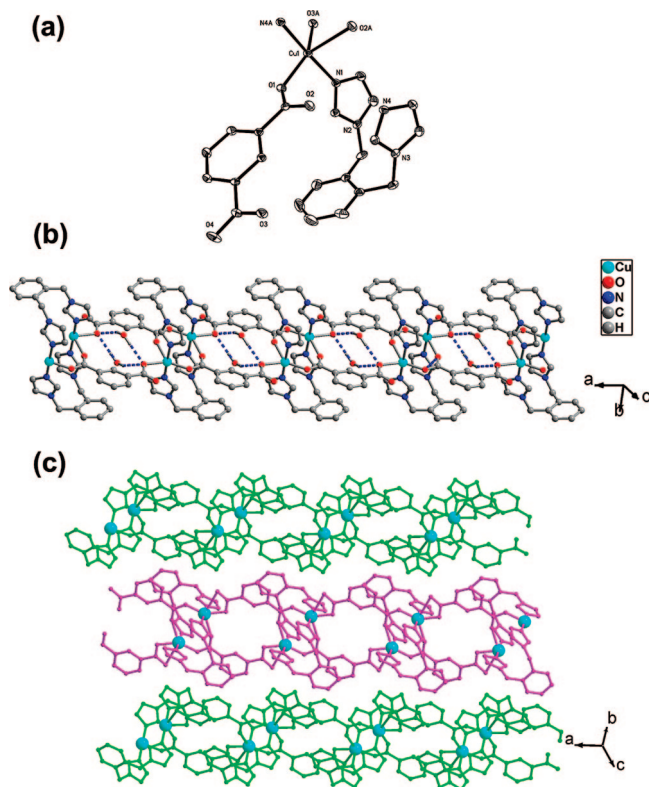


Figure 7. (a) The coordination environment of the Cu(II) center in compound 7, (b) the 1D looplike ladder structure of 7, and (c) the 2D supramolecular structure of 7 through the π - π interactions.

In **1** four lattice water molecules form a discrete acyclic water tetramer.^{10,11} Figure 1c displays the coordination environment of the acyclic water tetramer. Three water molecules ($O1w^i$, $O2w$, and $O4w^{ii}$) act as both hydrogen-bond donors and acceptors, while the $O3w$ molecule only acts as a hydrogen-bond donor. Moreover, the water tetramers are further stabilized through $O-H\cdots O$ (CO_3^{2-}) and $O-H\cdots N$ hydrogen-bonds. The hydrogen-bonds involving discrete water tetramers and the π - π interactions among the 1,2-bix ligands result in a 3D supramolecular structure of **1**.

In order to investigate the influence of the organic acid structure on the complex framework, six related organic acids (H_2L^1 , H_4L^2 , H_2L^3 , H_2L^4 , H_2L^5 , and H_2L^6) were used under the similar reaction conditions, and six new complexes **2–7** were obtained from the reaction systems. Compound **2**, $[Cu(L^1)(1,2-bix)_2] \cdot 2H_2O$, contains 2D (4,4) networks. Each Cu(II) center is six-coordinated by four nitrogen atoms ($N1$, $N1A$, $N4A$ and $N4B$) from four different 1,2-bix ligands, and two oxygen atoms ($O1$ and $O1B$) from two different L^1 ligands in a distorted octahedral geometry (Figure 2a). The 1,2-bix ligands, in *trans* conformations, bridge the Cu(II) centers to form two-strand 1D chains, which are further connected through L^1 ligands to generate 2D (4,4) networks, as illustrated in Figure 2b. The formation of (4,4) networks from 6-connecting centers in such a fashion is well-known.¹² In this 2D network, the lengths of the edges are not equivalent, and the intermetallic separations by L^1 and 1,2-bix are 12.02 and 9.59 Å, respectively. It is also worth noting that the Cu(II) \cdots Cu(II) separation by 1,2-bix in **2** is slightly longer than that in **1** due to the effect of the organic L^1 anion. Furthermore, hydrogen bonds involving the water molecules as donors and carboxylate oxygen atoms as acceptors help to stabilize and influence the structure of **2**, as shown in Figure 2b.

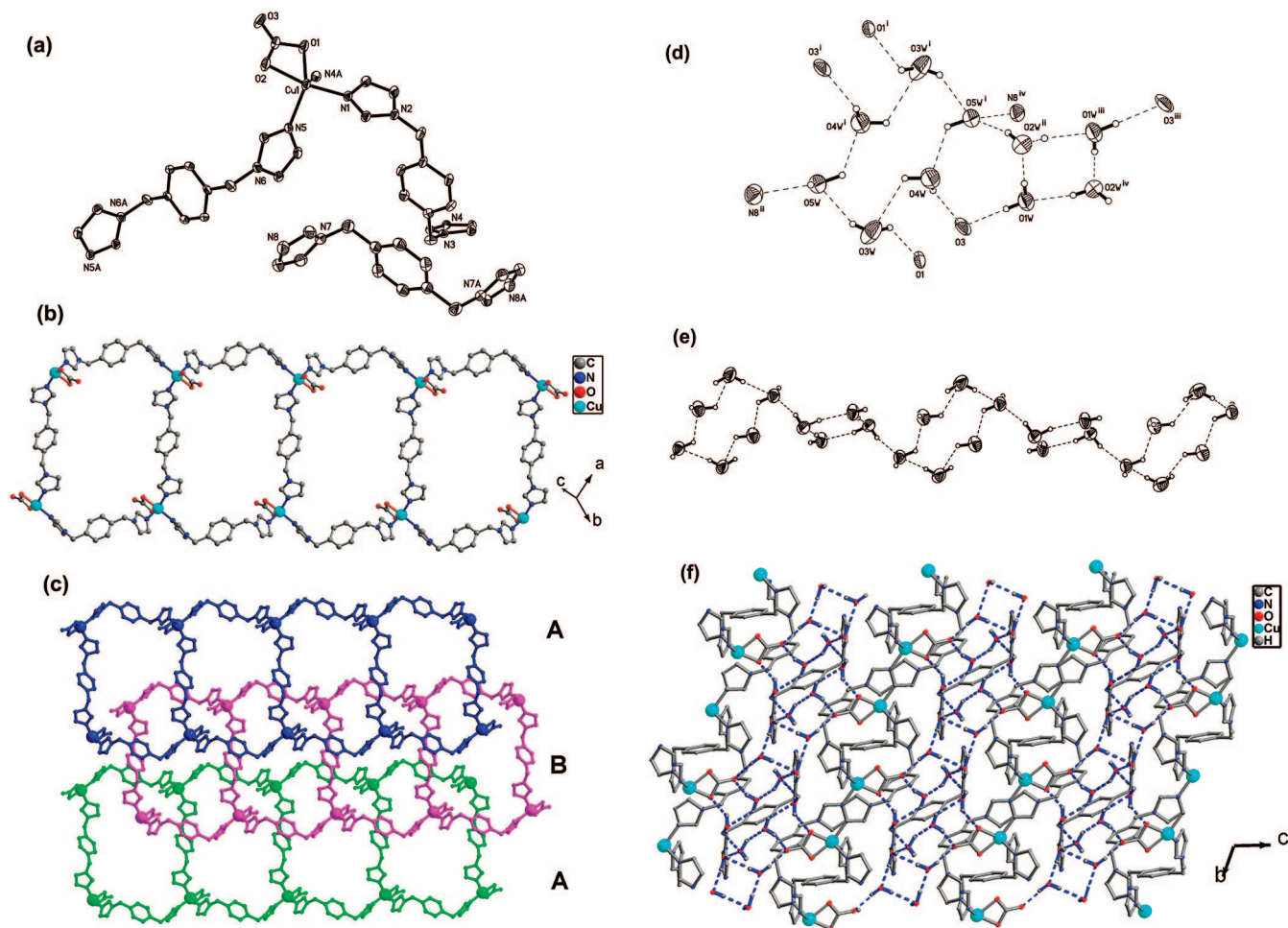


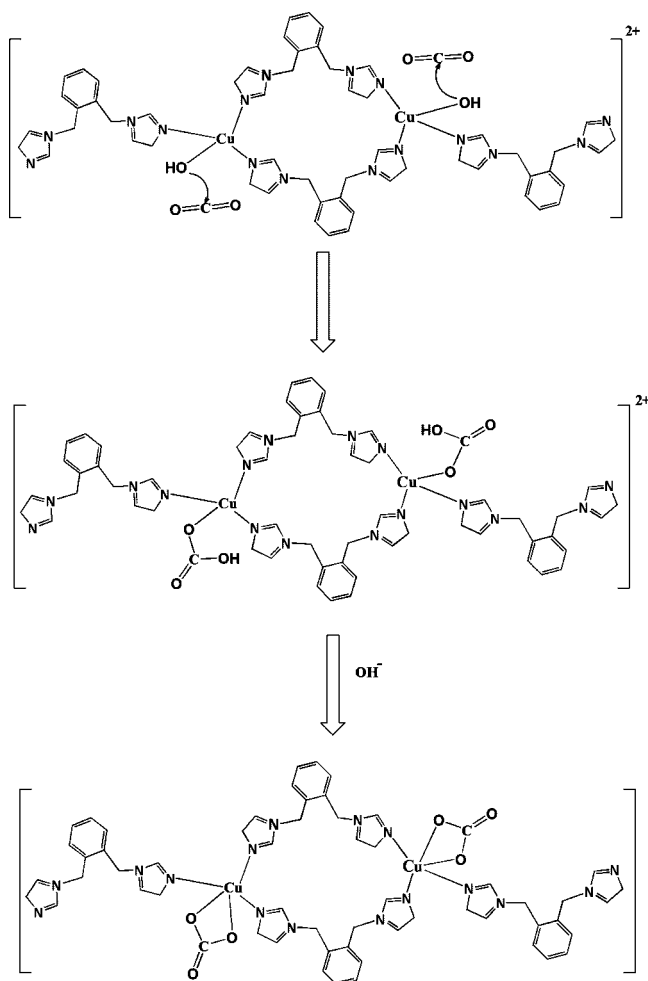
Figure 8. (a) The coordination environment of the Cu(II) center in compound **8**, (b) the 1D ladder structure of **8**, (c) the -ABAB- stacking sequence of 1D ladders in **8**, (d) the cyclic (H₂O)₄ and (H₂O)₆ water clusters and their coordination environments (symmetry code: (i) 1 - x, -y, -z; (ii) x, y - 1, z - 1; (iii) 1 - x, 1 - y, -z; (iv) 1 - x, 1 - y, 1 - z), (e) the 1D water chain built of the tetramers and hexamers, and (f) the 3D hydrogen-bonding structure of **8**.

In **3**, [Cu₂(L²)(1,2-bix)₂(H₂O)₄]·8H₂O, the Cu(II) cation adopts a distorted square-pyramidal geometry through coordinating to two nitrogen atoms from two 1,2-bix ligands, one oxygen atom from a L² anion, and two water molecules as shown in Figure 3a. Two nitrogen atoms (N1 and N3) and two oxygen atoms (O1 and O2w) constitute the base of the square-pyramid, whereas one water molecule (O1w) occupies the apical position with a Cu—O1w distance of 2.339(4) Å. The Cu(II) atoms are linked by the *trans*-form 1,2-bix ligands to generate singly bridged 1D chains, which is entirely different from the doubly bridged 1D chains in **2**. The L² ligands then link Cu(II) centers from two such neighboring 1D chains to create a 1D ladder structure (Figure 3b). The Cu(II)···Cu(II) distances in the ladder are 11.10 Å along the rungs and 9.65 Å along the sides.

In compound **4**, [Cu(1,2-bix)₂(H₂O)₂]·L³·4H₂O, the Cu(II) center displays a distorted octahedral geometry, and is coordinated to four nitrogen atoms (N2, N2A, N3A, and N3B) from four different 1,2-bix ligands, and two water molecules (O1w and O1wA) (Figure 4a). The Cu—N bond lengths are in the range of 2.008(2)–2.016(2) Å, and the N—Cu—N angles vary from 89.03(9) to 180. Each *trans*-form 1,2-bix links two Cu(II) atoms to generate an infinite 1D two-strand chain as illustrated in Figure 4b. The Cu(II)···Cu(II) separation across the *trans* 1,2-bix is 9.25 Å. The organic L³ anion does not coordinate to the Cu(II) center, but acts as a counteranion, and participates

in an extensive hydrogen bonding network which involves coordinated water molecules, all the free carboxylate oxygen atoms, and intercalated water dimers. In each water dimer (Figure 4c) an O2wⁱⁱ water molecule acts as a hydrogen-bond donor to both O1ⁱⁱ and O3w, while the O3w molecule, acting as a hydrogen-bond donor, is hydrogen-bonded to two neighboring O2 and O2ⁱ atoms, leading to a 3D supramolecular structure of **4** (Figure 4d).

The crystal structure of compound **5**, [Cu(L⁴)₂][Cu(1,2-bix)₂(H₂O)₂]·3H₂O, is comprised of two distinct and crystallographically independent motifs packed together (Figure 5a). A cationic chain, [Cu(1,2-bix)₂(H₂O)₂]²⁺, and a complex anion, [Cu(L⁴)₂]²⁻, form a perfectly complementary supramolecular pair with respect to charge. This is a rare example of a supramolecular stabilizing effect where neither partner is isolable in the absence of the other.¹³ One motif consists of one-dimensional (1D) two-strand cationic [Cu(1,2-bix)₂(H₂O)₂]²⁺ chains, in which the Cu(II) atoms are six-coordinated by four nitrogen atoms from four *trans*-form 1,2-bix ligands, and two water molecules in a distorted octahedral geometry. The four nitrogen atoms (N1, N1A, N4A, and N4B) occupy the equatorial positions, whereas the two water molecules (O1w and O1wA) occupy the axial positions with a Cu—O1w distance of 2.45 Å. The Cu(II)···Cu(II) separation bridged by *trans*-form 1,2-bix in the 1D chain is 8.75 Å, which is much shorter than that observed in **4** (Figure 5b).

Scheme 2. A Possible Mechanism for the Fixation of Carbon Dioxide and Formation of 1

The second motif of **5** is composed of anionic $[\text{Cu}(\text{L}^4)_2]^{2-}$ complexes, each involving one Cu(II) atom and two chelating L^4 ligands (Figure 5a). The Cu(II) coordination is square-planar, with four oxygen atoms from two L^4 . The bond distances $[\text{Cu}(2)-\text{O}(1) = 1.913(3)$ and $\text{Cu}(2)-\text{O}(3) = 1.935(3)$ Å and bond angles involving the Cu(II) cations are similar to those found in other Cu(II) complexes.^{3f-h} An interesting aspect of this structure is the presence of the water dimer ($\text{O}2\text{w} \cdots \text{O}3\text{w}$) in the lattice. The water molecules are also involved in hydrogen bonding interactions with carboxylate groups bound to the Cu(II) center, resulting in a 3D supramolecular structure (Figure 5c,d).

As shown in Figure 6a, in compound **6**, $[\text{Cu}(\text{L}^5)(1,2\text{-bix})] \cdot \text{H}_2\text{O}$, the Cu(II) center is coordinated by two oxygen atoms ($\text{O}1$ and $\text{O}3\text{A}$) from two distinct L^5 , and two nitrogen atoms ($\text{N}3$ and $\text{N}1\text{A}$) from two different 1,2-bix ligands in a slightly distorted square-planar coordination sphere. The average Cu–O and Cu–N distances are 1.96 and 1.99 Å, respectively. Two 1,2-bix ligands in *cis* conformations bridge two Cu(II) atoms to generate a $[\text{Cu}_2(1,2\text{-bix})_2]^{4+}$ unit with the Cu(II)···Cu(II) separation of 3.55 Å. The adjacent $[\text{Cu}_2(1,2\text{-bix})_2]^{4+}$ units are further linked via the L^5 ligands to form a 1D looplike ladder structure (Figure 6b). The Cu(II)···Cu(II) separation for the L^5 -bridging edge is 9.01 Å, which is significantly shorter than that in compound **3**.

In compound **7**, $[\text{Cu}_2(\text{L}^6)_2(1,2\text{-bix})_2] \cdot \text{H}_2\text{O}$, the Cu(II) atom is five-coordinated by three oxygen atoms ($\text{O}1$, $\text{O}2\text{A}$ and $\text{O}3\text{A}$) from three L^6 ligands, and two nitrogen atoms ($\text{N}1$ and $\text{N}4\text{A}$) from two 1,2-bix ligands in a distorted trigonal-bipyramidal

geometry (Figure 7a). The average Cu–N distance of 1.96 Å is similar to that in **6**, while the average bond distance (2.11 Å) between carboxylate oxygen atoms and Cu(II) atoms is slightly longer than those in **6**. Each L^6 ligand bridges three Cu(II) centers through its carboxylate groups, leading to a looplike ladder structure with Cu(II)···Cu(II) separations of 10.08 Å for the L^6 -bridging edge and 4.01 Å for the 1,2-bix-bridging edge (Figure 7b). Furthermore, the $\text{O}1\text{w}$ molecule is involved in hydrogen bonding with the carboxylate oxygen atoms, stabilizing the ladder structure. The benzene rings from neighboring ladders are paired to furnish slightly weak π – π interactions (centroid-to-centroid distance of 3.84 Å, face-to-face distance of 3.69 Å, and dihedral angle of 12.06°). When this interaction is taken into account, the 1D ladders are assembled into a 2D network (Figure 7c).

When 1,4-bix was used instead of 1,2-bix under similar synthetic conditions as for **1**, structurally different 1D ladders were formed in compound **8**, $[\text{Cu}_2(\text{CO}_3)_2(1,4\text{-bix})_3] \cdot (1,4\text{-bix}) \cdot 10\text{H}_2\text{O}$. The Cu(II) center displays a distorted square-pyramidal geometry, and is coordinated by two oxygen atoms from one CO_3^{2-} anion, and three nitrogen atoms from three different 1,4-bix ligands, which is the same as that in **1** (Figure 8a). Two nitrogen atoms ($\text{N}1$ and $\text{N}5$) and two oxygen atoms ($\text{O}1$ and $\text{O}2$) constitute the base of the pyramid, whereas one nitrogen atom ($\text{N}4\text{A}$) occupies the apical position with a Cu–N distance of 2.149(3) Å. The Cu(II) atoms are bridged by 1,4-bix ligands to form a 1D ladder structure rather than the dimer observed in complex **1** (Figure 8b). The Cu(II)···Cu(II) distances in the ladder are 14.46 Å along the rungs and 12.65 Å along the sides. The 1D ladders repeat in an -ABAB- stacking sequence instead of the -AA- stacking fashion (Figure 8c).¹³

Water clusters and tapes have been extensively studied in recent years.¹⁴ In compound **8**, water hexamers and tetramers are linked through $\text{O}2\text{w}^{\text{ii}}-\text{H} \cdots \text{O}5\text{w}^{\text{i}}$ hydrogen bond and their symmetric equivalents to produce an extended water chain (Figure 8d,e).^{15–19} Furthermore, the oxygen atoms from the CO_3^{2-} anion, and a nitrogen atom from the free 1,4-bix ligand form hydrogen bonds with the water molecules, leading to a 3D supramolecular structure (Figure 8f).

The structure of compound **9**, $[\text{Cu}(\text{L}^6)_2(1,4\text{-bix})][\text{Cu}(1,4\text{-bix})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$, is shown in Figure 9a. Surprisingly, it consists of two types of coordination polymers: 2D (4,4) grids of $[\text{Cu}(1,4\text{-bix})_2(\text{H}_2\text{O})_2]^{2+}$ **A**, and linear chains of $[\text{Cu}(\text{L}^6)_2(1,4\text{-bix})]^{2-}$ **B**. The cationic component **A** forms a simple 2D (4,4) grid with grid dimensions of 13.57×13.77 Å (Figure 9b). The vertices are octahedral Cu(II) centers with equatorial planes filled by four N atoms from four different 1,4-bix ligands, and axial sites filled by two water molecules. Component **B** is the coordination polymer anion, $[\text{Cu}(\text{L}^6)_2(1,4\text{-bix})]^{2-}$, where the Cu(II) center has a square-planar geometry and coordinated by two nitrogen atoms from two 1,4-bix ligands, and two oxygen atoms from two L^6 ligands (Figure 9c). The Cu(II) atoms are bridged by 1,4-bix ligands to form linear chain structures with Cu(II)···Cu(II) separation of 13.57 Å, whereas the L^6 ligands are attached to both sides of the chain in a monodentate fashion (Figure 9d,e). The use of a coordination polymer anion for a coordination network is unusual.²⁰ In this case, the size of the anion prevents the formation of interpenetrating networks. The complex counteranion **B** itself is not isolable but is stabilized in the crystal lattice in the presence of the cationic (4,4) sheets of **A**. This is an unusual example of a mutual host–guest stabilization effects in a coordination framework, as neither component exists in the absence of the other.²¹

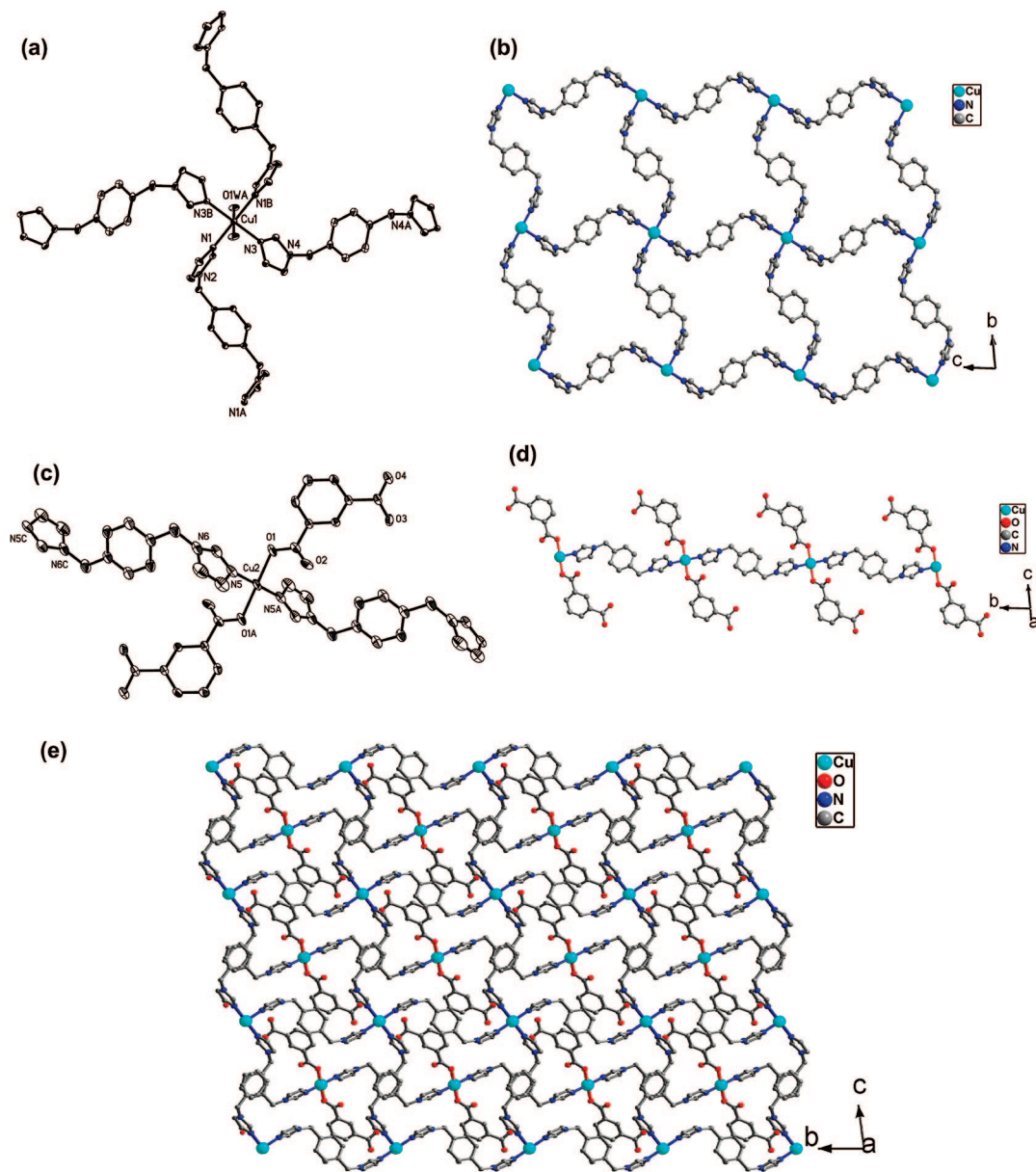


Figure 9. (a) The coordination environment of the Cu(II) center in the $[\text{Cu}(\text{1,4-bix})_2(\text{H}_2\text{O})_2]^{2+}$ cation, (b) the 2D network structure of the $[\text{Cu}(\text{1,4-bix})_2(\text{H}_2\text{O})_2]^{2+}$ cations, (c) the coordination environment of the Cu(II) center in the $[\text{Cu}(\text{L}^6)_2(\text{1,4-bix})]^{2-}$ anion, (d) the 1D chain structure of the $[\text{Cu}(\text{L}^6)_2(\text{1,4-bix})]^{2-}$ anions, and (e) the 2D structure of **9**.

As mentioned above, each Cu(II) center in the grid has two coordinating water molecules. The uncoordinated carboxylate groups of the $[\text{Cu}(\text{L}^6)_2(\text{1,4-bix})]^{2-}$ anions form strong hydrogen bonds with the coordinated water molecules of the $[\text{Cu}(\text{1,4-bix})_2(\text{H}_2\text{O})_2]^{2+}$ cations. For example, the distance of 2.712 Å between O1w and the carboxylate O3 atom indicates the formation of an $\text{O}-\text{H}\cdots\text{O}$ hydrogen bond, although the hydrogen atoms of the water molecule could not be found. These hydrogen-bond interactions result in an overall 3D supramolecular structure.

Effect of Organic Acid on the Structure of the Compound. The organic anions play a crucial role in determining the molecular structures of the resultant complexes **1–7**. In this study, the structural features of the organic anions such as shape, flexibility, and length of the spacers are the underlying reason for the structural differences within this series of Cu(II) complexes. To investigate the influence of organic anion ligands on the complex structures, three aromatic acid ligands H_2L^1 , H_4L^2 , and H_2L^6 were used. Although compounds **2**, **3**, and **7**

were synthesized under similar conditions, their structures are very different. The common feature of the three ligands is their planarity, and each contains large aromatic groups. Both H_2L^1 and H_2L^6 are dicarboxylic acid ligands, while the H_4L^2 is a tetracarboxylic acid ligand. For H_2L^1 and H_2L^6 , the two carboxylate groups of H_2L^1 are located in the para positions of benzene ring, whereas those of H_2L^6 are in the meta positions. In addition, H_2L^1 has a larger conjugated π -system from the additional benzene ring. When H_4L^2 was used in the self-assembly process, its four carboxylic acid groups are all deprotonated, and only two are coordinated to the Cu(II) centers. Although two para carboxylate groups of L^2 coordinate to Cu(II) centers in a similar bidentate mode to L^1 , two quite different metal-organic architectures of **2** and **3** were obtained. The structural differences between **7** relative to **2** and **3** showed the importance of the dicarboxylic acid position on the complex construction. In order to study the effect of the spacer length ($-\text{CH}_2-$) and flexibility of fatty acid ligands on the complex

structures, typical fatty acids such as H_2L^3 , H_2L^4 , and H_2L^5 were used under similar synthetic conditions. The H_2L^3 ligand possesses flexibility owing to the presence of $-\text{CH}_2-$ spacers between the two carboxylate groups. However, in contrast with H_2L^3 , H_2L^4 and H_2L^5 show relatively rigid coordination properties due to the presence of $-\text{CH}=\text{CH}-$ spacers between the two carboxylate groups.²² The only structural difference between H_2L^4 and H_2L^5 is the conformation of the two carboxylate groups. These geometrical differences in the fatty acids result in the formation of **4–6** with quite distinct architectures under similar synthetic conditions.

The organic anions also have an important effect on the conformation of the bix ligands. Generally, the flexible ligand bix is capable of adopting either *cis* or *anti* conformations depending on the orientation of the two imidazole arms (Scheme 1), which will result in different structures. As can be seen in complexes **1–5** and **8–9**, the bix ligands bridge Cu(II) cations exclusively through the *anti* conformation, whereas the *cis* conformation was observed in **6** and **7**. This observation indicates that the conformation of the bix is strongly dependent upon the organic anions used. In other words, the effects of organic anions are apparently related to the flexibility of the bix ligands. In addition, bix may show both *cis* and *anti* conformations in the same molecule such as in the reported complexes $\text{Ag}_2(\text{bix})_3(\text{NO}_3)_2$, $[\text{Zn}(\text{bix})_2(\text{NO}_3)_2] \cdot 4.5\text{H}_2\text{O}$ and $[\text{Co}(\text{bix})_2(\text{H}_2\text{O})_2](\text{SO}_4) \cdot 7\text{H}_2\text{O}$.^{6a,b,20a} Moreover, interpenetration is observed in above three structures constructed only with bix. However, in complexes **1–9**, the interpenetrating ability of bix ligands is disabled. We believed that the presence of the organic anions act as a key role in the generation of such structures.

In addition, complexes **1** and **8** demonstrate the effect of the imidazole position of bix on the complex structures. Compound **1**, with a dimeric structure, was synthesized by mixing $\text{Cu}(\text{OH})_2$ and 1,2-bix, while compound **8**, with a 1D ladder structure, was obtained using 1,4-bix instead of 1,2-bix under similar conditions.

Fixation of Atmospheric Carbon Dioxide. Treatment of a mixture of 1,2-bix or 1,4-bix with $\text{Cu}(\text{OH})_2$ in an ammonia solution gave the unexpected carbonate (CO_3^{2-}) complex $[\text{Cu}_2(\text{CO}_3)_2(1,2\text{-bix})_4] \cdot 8\text{H}_2\text{O}$ **1** or $[\text{Cu}_2(\text{CO}_3)_2(1,4\text{-bix})_3] \cdot (1,4\text{-bix}) \cdot 10\text{H}_2\text{O}$ **8** by slow evaporation at room temperature. This result indicates that the reaction system absorbed carbon dioxide from air to convert it into the carbonate.²³ It should be noted that the chemistry of carbon dioxide (CO_2) has received much attention recently because of its potential use as an abundant carbon source and its indirect role as an environmental pollutant.²⁴ In particular, the fixation of atmospheric carbon dioxide into metal-organic compounds is very important from an environmental point of view.²⁵ So far, a few examples of spontaneous fixation of CO_2 by metal complexes are known in the literature. As far as our Cu(II) complexes are concerned, the presence of externally added ammonia is necessary to bring about fixation of carbon dioxide. If the reaction is performed without addition of ammonia, compounds **1** and **8** can not be obtained. A tentative mechanism for the production of carbonate from carbon dioxide and generation of **1** is shown in Scheme 2.^{23–26} First, the ammonia transforms into ammonium cations and hydroxyl anions. Second, the hydroxyl anions react with carbon dioxide to give the Cu(II) bicarbonate complex. Finally, additional hydroxyl anions react with bicarbonate anions to form the carbonate ligand. This mechanism is widely acceptable in

biological systems, where the Zn(II) cation containing carbonic anhydrase fixes carbon dioxide as bicarbonate at $\text{pH} \sim 7$.^{25,26}

Conclusion

Nine new complexes with different framework structures were rationally designed via the self-assembly of two structurally related flexible bis(imidazole) ligands with Cu(II) salts and various organic acids. The structures of the complexes are profoundly influenced by the organic anions: from the arm-shaped dinuclear complex, the 1D structures including chains and ladders, to the 2D networks. The structural features of the organic anions such as shape, flexibility and length of the spacers are the main reason for the structural differences of the Cu(II) complexes. A water dimer, tetramer and chain were also identified in the series of Cu(II) complexes. The water clusters associated with crystal hosts in these complexes help to stabilize their complex structures. The carbonate complexes **1** and **8** indicate that the reaction system absorbed carbon dioxide from air to convert it into the carbonate.

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Supporting Information Available: Nine X-ray crystallographic files (CIF) and the simulated and experimental X-ray powder diffraction patterns for compounds **1–9** are available free of charge via the Internet at <http://pubs.acs.org>.

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