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Hydrogen bond induced change of geometry and crystallized form of copper(II) complexes: syntheses and crystal structure of complexes with Schiff-base ligands containing two imidazolyl groups

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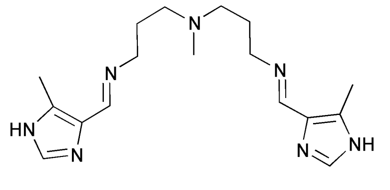
Copper(II) complexes with the Schiff base methylbis[3-(5-methylimidazol-4-ylmethyleneimino)propyl]amine (BDPA), $[Cu(BDPA)][ClO_4]_2\cdot H_2O$ **1** and $[Cu(BDPA)][PF_6]_2$ **2**, and with a deprotonated Schiff base ligand [H_2BIPO = 1,3-bis[(5-methylimidazol-4-ylmethyleneimino)propan-2-ol], $\{[Cu(HBIPO)]ClO_4\cdot H_2O\}_n$ **3** and **4**, have been prepared. Single-crystal structures show that **1** adopts a distorted square-pyramidal geometry with the basal plane occupied by an imidazole nitrogen, two imines and one amino nitrogen atom and the apical position by another nitrogen atom from BDPA. **2** adopts a distorted trigonal-bipyramidal geometry with two imidazole nitrogen atoms at axial positions. Both **3** and **4** adopt distorted square-pyramidal geometry with four nitrogen atoms from HBIPO in the basal plane and the apical position occupied by a deprotonated imidazole nitrogen atom from an adjacent [Cu(HBIPO)] unit, resulting in polynuclear complexes. The differences in geometry and crystallization pathway between **1** and **2**, and **3** and **4**, are discussed based on the crystal structures, indicating that hydrogen bonding to the basal plane imidazole group plays an important role both in the change of geometry and crystallization form of the copper(II) complexes.

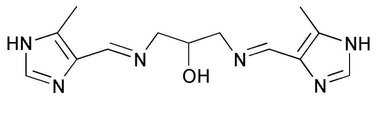
Introduction

Hydrogen bonds play a key role in metalloenzyme catalytic processes. A case in point is that, in carbonic anhydrase II (CAII), the hydrogen bonds involving Gln-92 and Glu-117 exert a subtle yet important influence on protein–zinc affinity, the pK_a value, and reactivity of Zn-bound solvents.[1–3] The imidazole group, because of its existence in almost all copper proteins, has received great interest both in synthetic models for copper protein active sites[4–10] and in the recognition of copper ions.[11,12] Recently, the deprotonation of an imidazole group was used to assemble various kinds of supramolecule, including 1-D zig-zag chains,[13,14] 1-D helical chains,[15] 1-D homochiral and heterochiral zig-zag chains,[16] cyclic tetramer[14,16] and cyclic hexamer[17] copper complexes. Although copper–imidazole complexes were extensively studied, to our knowledge few investigations have been reported on the hydrogen bond interactions with metal bound ligands in copper–imidazole complexes. As the direct protein ligands of transition-metal sites in proteins are typically nested in a hydrogen-bond network,[18,19] the entire proteins, in addition to the metal bound ligands, may affect the stability and chemical properties of the protein–metal complex by modulating hydrogen bond–ligand–metal interaction. Therefore, investigation of this hydrogen bonding may help our understanding of structure/function relationships of some metal enzymes.

In our recent papers[20] on metal complexes involving the imidazole group we reported the effect of hydrogen bonding on zinc coordination geometry. As parts of this work and as systematic studies on metal–imidazole complexes,[6,20,21] we present here the synthesis and crystal structures of $[Cu(BDPA)][ClO_4]_2\cdot H_2O$ **1**, $[Cu(BDPA)][PF_6]_2$ **2**, $\{[Cu(HBIPO)]ClO_4\cdot H_2O\}_n$ **3** and **4** (BDPA = methylbis[3-(5-methylimidazol-4-ylmethyleneimino)propyl]amine, H_2BIPO = 1,3-bis(5-methylimidazol-4-ylmethyleneimino)propan-2-ol, Scheme 1). The difference in geometry and crystallization forms between **1** and **2**, and between **3** and **4**, is discussed, focusing on hydrogen bond interaction with the metal-bound ligands.



Structure of the BDPA ligand



Structure of the H_2BIPO ligand

Scheme 1 Structures of H_2BIPO and BDPA ligands.

Experimental

All reagents in the synthetic reaction were commercially available and used as received. All samples were thoroughly dried prior to elemental analyses.

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Physical measurements

The C, H and N elemental analyses were performed on a Perkin-Elmer 204 elemental analyzer.

CAUTION: perchlorate salts of metal complexes are potentially explosive and should be handled in small quantity with care.

Preparations

(a) [Cu(BDPA)][ClO$_4$]$_2$·H$_2$O 1. To a solution of 5-methyl-4-imidazolecarbaldehyde (0.22 g, 2 mmol) in methanol (10 mL) was added bis(3-aminopropyl)methylamine (0.15 g, 1 mmol). The solution was refluxed at 60–70 °C for 20 min with stirring. Then a solution of $Cu(NO_3)_2\cdot H_2O$ (0.29 g, 1 mmol) and $NaClO_4\cdot H_2O$ (0.28 g, 2 mmol) in methanol (10 mL) was added. The reaction turned blue immediately. It was allowed to stand in air at room temperature for a week, and blue crystals of complex **1** were obtained in 67% yield (0.41 g). Calc. for $C_{17}H_{29}Cl_2CuN_7O_9$ (%): C, 33.45; H, 4.75; N, 16.06. Found (%): C, 33.51; H, 4.95; N, 15.87.

(b) [Cu(BDPA)][PF$_6$]$_2$ 2. Complex **2** was prepared in a similar way to that of **1**, except using $NaPF_6$ instead of $NaClO_4\cdot H_2O$. Yield 78% (0.53 g). Calc. for $C_{17}H_{27}CuF_{12}N_7P_2$ (%): C, 29.87; H, 3.95; N, 14.35. Found (%): C, 29.41; H, 3.67; N, 14.51.

(c) {[Cu(HBIPO)]ClO$_4$·H$_2$O}$_n$ 3. The Schiff base ligand (H_2BIPO) was prepared as previously.[6a] A methanol solution of $Cu(NO_3)_2\cdot H_2O$ (0.297 g, 1 mmol) and $NaClO_4\cdot H_2O$ (0.28 g, 2 mmol) was added dropwise to an ethanol (10 mL) solution of H_2BIPO (0.274 g, 1 mmol) while stirring. The resulting solution turned green, after adjusting the pH value to 8–9 with NaOH in methanol. Green prismatic crystals, suitable for X-ray crystallography, were obtained within a day. Yield 71% (0.322 g). Calc. for $C_{13}H_{18}ClCuN_6O_6$ (%): C, 34.4; H, 3.97; N, 18.53. Found (%): C, 34.0; H, 4.1; N, 18.81.

(d) {[Cu(HBIPO)]ClO$_4$·H$_2$O}$_n$ 4. Complex **4** was prepared similarly to **3**, except using 1,3-diaminopropan-2-ol instead of NaOH to adjust the pH value of the solution. Yield 64% (0.29 g). Found (%): C, 34.7; H, 4.4; N, 18.1.

Crystallography

Diffraction intensities for the four copper complexes were collected at 295 K on a Siemens R3m or CCD diffractometer. Lorentz-polarization and absorption corrections were applied. Structural solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS 97 and SHELXL 97 program packages, respectively.[22,23] Complex **4** crystallized in a chiral space group, and its absolute structure was determined with a Flack parameter of 0.02(8).[24] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the organic ligands were generally geometrically placed (C–H 0.96 Å) and those of the aqua ligands located from the difference maps; all were assigned the same isotropic thermal parameters and included in the structure-factor calculations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections incorporated.[25] Crystallographic data are summarized in Table 1. Selected bond lengths are given in Table 2.

CCDC reference number 186/2336.

See http://www.rsc.org/suppdata/dt/b0/b007415m/ for crystallographic files in .cif format.

Results and discussion

Crystal structures

(a) [Cu(BDPA)][ClO$_4$]$_2$·H$_2$O 1. An ORTEP[26] view of the molecular structure of complex **1** is shown in Fig. 1 and the coordination mode of copper(II) is shown in Scheme 2. Complex **1** consists of a dicationic copper(II) complex, two perchlorate anions and one lattice water molecule. The copper(II) ion has five-coordination with a quinquedentate BDPA ligand containing two imidazole nitrogen atoms N(1) and N(7), two imines and one amino nitrogen atom. The structural index parameter (τ)[27] is 0.36, indicating that the geometry around the Cu^{II} is close to a square pyramid. The basal positions are occupied by an imidazole nitrogen atom N(1), two imines and one amino nitrogen atom, and the apical position is occupied by an imidazole nitrogen atom N(7). It is noteworthy that the two Cu–N(imidazole nitrogen) bond lengths are different: Cu–N(1) [2.032(4) Å] is much shorter than Cu–N(7) [2.187(4) Å], as in the copper(II) complex with bis[3-(imidazol-4-ylmethyleneimino)propyl]amine previously reported.[13] In **1** the undeprotonated nitrogen atom N(2) as proton donor forms moderately strong hydrogen bonds with O(14a) [N(2)···O(14a) 2.939(8) Å], while the undeprotonated nitrogen atom N(6) as proton donor is hydrogen-bonded to O(1w) and O(21) [N(6)···O(1w) 2.965(7), N(6)···O(21) 2.961(8) Å]. These hydrogen bonds play an important role at the supramolecular level. As shown in Fig. 2, the lattice water links N(6) and O(14a) by hydrogen bonds to form a one-dimensional helical chain.

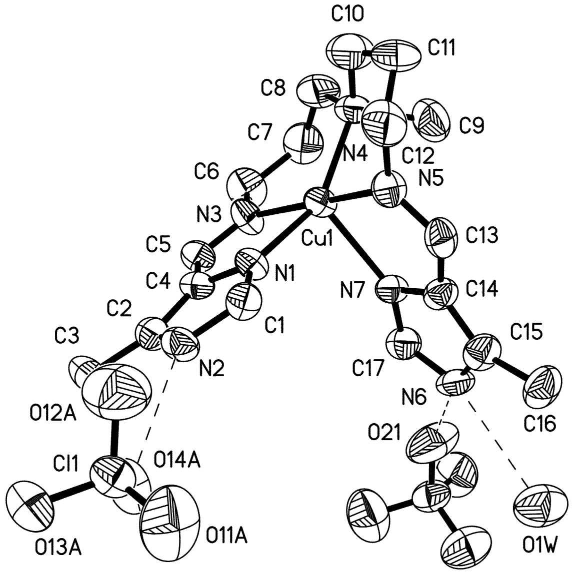


Fig. 1 ORTEP plot showing the structure of the dication and hydrogen bond scheme in complex **1**.

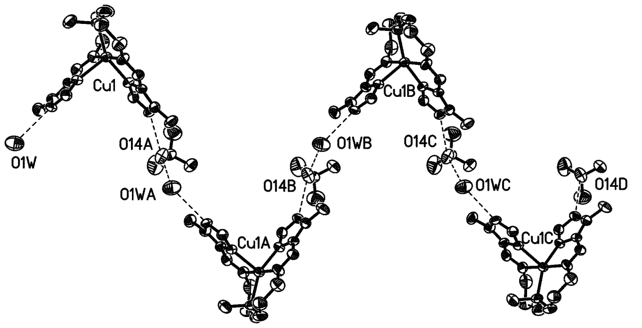


Fig. 2 ORTEP plot showing the helical chain linked by hydrogen bonds in complex **1**.

(b) [Cu(BDPA)][PF$_6$]$_2$ 2. An ORTEP view of the molecular structure of complex **2** is shown in Fig. 3. Complex **2** consists of a dicationic copper(II) complex and two PF_6^- anions. Similar to **1**, each Cu^{II} is also five-coordinated with five N donor atoms from BDPA, but the geometry is close to a trigonal bipyramid with two imidazole nitrogens at axial positions, because the

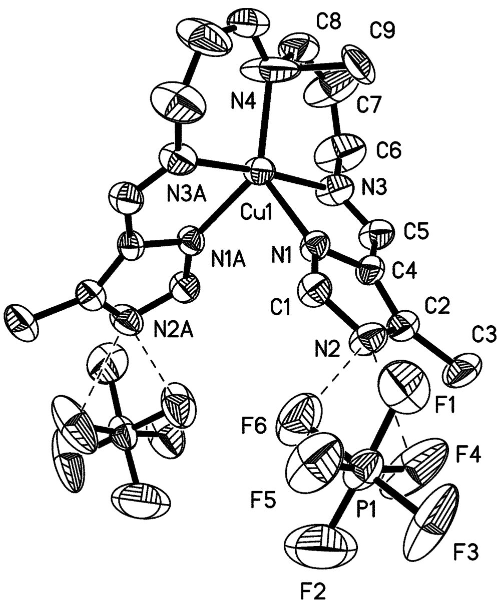


Fig. 3 ORTEP plot showing the structure of the dication and hydrogen bond scheme in complex **2**.

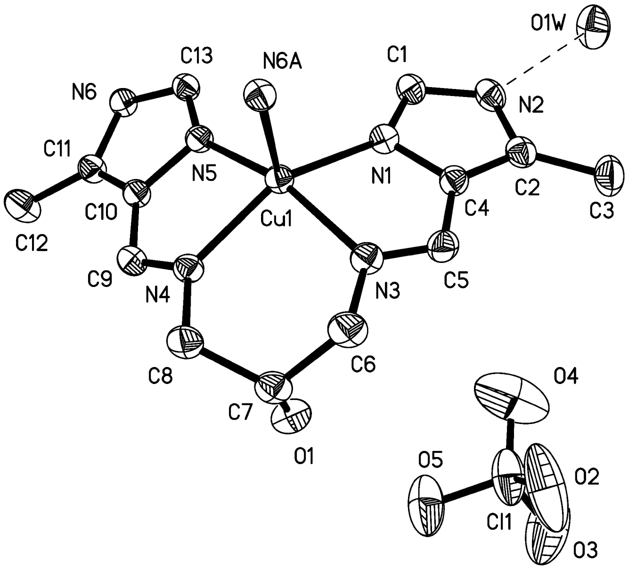
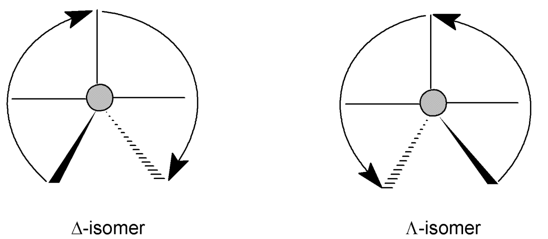


Fig. 4 ORTEP plot showing the structure of the dication and hydrogen bond scheme in complex **3**.

value of τ is 0.73. The most important feature in complex **2** is that the two Cu–$N_{imidazole}$ bond distances are identical [Cu–N(1) = Cu–N(1a) 2.114(4) Å]. Both undeprotonated nitrogen atoms of the imidazole group form weak hydrogen bonds with F(4) and F(6) [N(2)···F(4a) = N(2a)···F(4) 3.006(7), N(2)···F(6a) = N(2a)···F(6) 2.970(7) Å].

Owing to the spiral coordination arrangement of the coordinated ligand around Cu^{II}, the dications in complexes **1** and **2** are assumed to be the Δ or Λ enantiomorph defined[15] as shown in Chart 1. As **1** and **2** crystallized in the centrosymmetric space groups $P2_1/c$ and $C2/c$, respectively the Δ and Λ enantiomorphs of the cation coexist as the racemic form in the crystal.



Δ-isomer

Λ-isomer

Chart 1

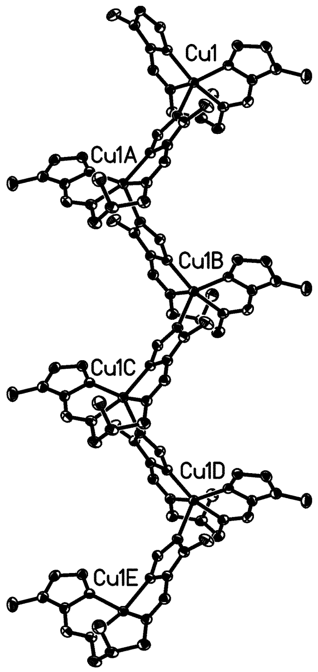
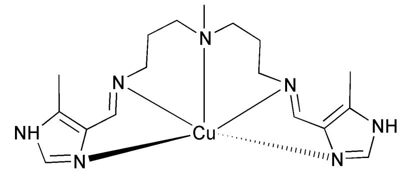
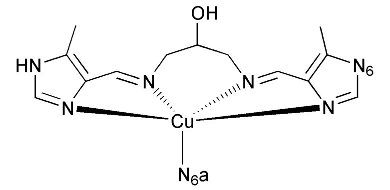


Fig. 5 One-dimensional helical chain in complex **3**.

(c) $\{[Cu(HBIPO)]ClO_4 \cdot H_2O\}_n$ 3. An ORTEP view of the molecular structure of complex **3** is shown in Fig. 4 and the coordination mode in Scheme 2. **3** consists of a mono-positive copper(II) complex, a perchlorate anion, and a lattice water molecule. The coordination geometry of Cu^{II} is very close to a square pyramid, because the τ value is 0.137. Its basal plane is occupied by the 4 N donor atoms of the monodeprotonated HBIPO ligand, and the apical position is occupied by the N(6a) atom of an adjacent and symmetry-related $(-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2})$ fragment. This arrangement gives rise to a polynuclear helical structure of [Cu(HBIPO)] units as shown in Fig. 5, in which copper(II) ions are sequentially bridged by imidazolate groups, very similar to the zig-zag chain copper(II) complex with 1,4-bis(imidazol-4-ylmethyleneimino)butane.[14] The Cu–N bond lengths in basal positions are in the range between 1.998(3) and 2.047(4) Å, much shorter than the Cu–N bond length in apical position [2.180(3) Å]. The oxygen atom of the lattice water molecule, as proton acceptor, forms hydrogen bonds with N(2) [N(2)···O(1w) 2.735(4) Å] and O(1)



Coordination mode of the copper(II) ion in complex 1



Coordination mode of the copper(II) ion in complex 3

Scheme 2 Coordination mode of complexes **1** and **3**.

Table 1 Crystal data and structure refinement for complexes **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{17}H_{29}Cl_2CuN_7O_9$	$C_{17}H_{27}CuF_{12}N_7P_2$	$C_{13}H_{18}ClCuN_6O_6$	$C_{13}H_{18}ClCuN_6O_6$
Formula weight	609.91	682.94	453.32	453.32
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/n$	$P2_1$
a/Å	18.038(4)	20.424(4)	12.056(2)	9.620(2)
b/Å	8.589(2)	8.6320(9)	10.058(2)	10.045(2)
c/Å	18.183(4)	18.313(4)	15.141(3)	9.699(2)
β/°	113.62(3)	122.16(3)	90.58(3)	102.87(3)
V/Å^3	2581.1(1)	2733.2(9)	1835.9(6)	913.7(3)
Z	4	8	4	2
μ(Mo-Kα)/mm^{-1}	1.112	1.020	1.379	1.386
Measured reflections	3232	2983	2644	1742
Observed reflections [$I > 2\sigma(I)$]	2065	2186	2088	1111
$R1$ [$I > 2\sigma I$]	0.0779	0.0796	0.0364	0.0773
$R2$ (all data)	0.2424	0.2434	0.1023	0.2135

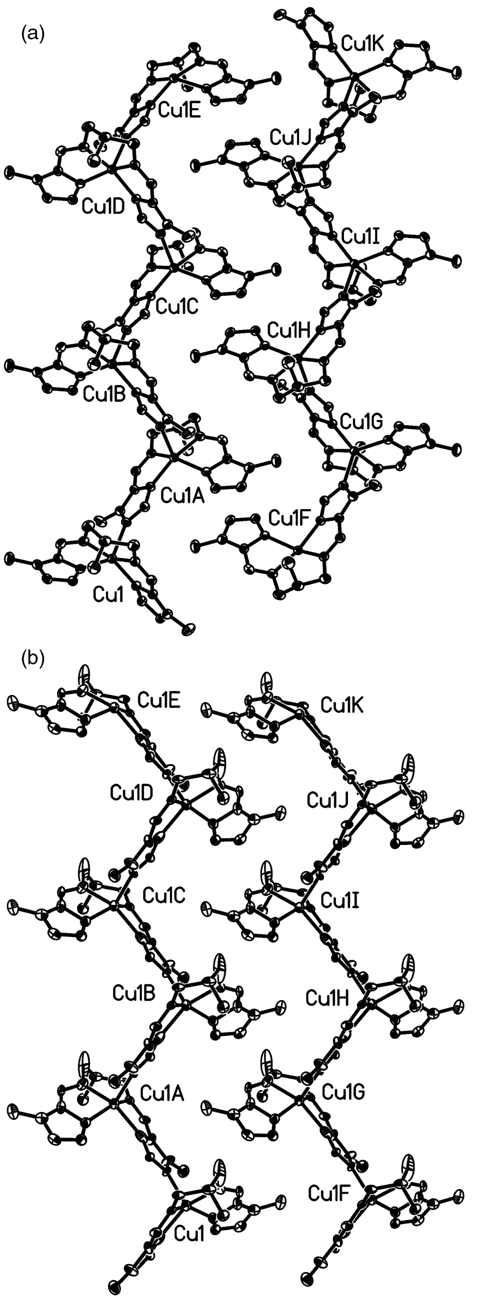


Fig. 6 (a) Two adjacent helical chains arranged in opposite directions in crystal **3**. (b) Two adjacent helical chains arranged in the same direction in crystal **4**.

[O(1w) ⋯ O(1) 2.762(4) Å] atoms from the ligand, respectively. These lead to two adjacent chains arranged in opposite directions in complex **3**.

(d) {[Cu(HBIPO)]ClO$_4$·H$_2$O}$_n$ 4. Despite being very similar to complex **3** in structure and geometry ($\tau = 0.135$) and even identical in formula, it is noteworthy that there is a dramatic difference in Cu–N bond distances both in the basal plane and at the apical position between **3** and **4**. The bond length of Cu–N(5) in the basal plane in **3** is 0.16 Å shorter than that of **4**, while Cu–N(6) at the apical position in **3** is 0.13 Å longer than that in **4**. In addition the lattice water molecule is only hydrogen-bonded to a hydroxyl group in the HBIPO ligand.

The most interesting feature in complexes **3** and **4** is at the supramolecular level. As shown in Fig. 6, the two adjacent helical chains in **3** are arranged in opposite directions at intervals, while in **4** all helical chains are arranged in the same direction. Therefore, **4** can be considered as the resulting auto-resolution product of **3**, due to **3** and **4** crystallizing in centrosymmetric ($P2_1/n$) and chiral space groups ($P2_1$) respectively.

Modification of hydrogen bonds

Comparing complexes **1** and **2**, it was found that the hydrogen bonds to the imidazole group play a key role in the alteration of geometry around copper(II). As shown in Table 2, when the hydrogen bonds of the two undeprotonated N(2) and N(6) atoms are different in strength, the two Cu–N$_{\text{imidazole}}$ bond distances are dramatically changed, the bond length of Cu(1)–N(1) [2.032(4) Å] in **1** being significantly shorter than that of Cu(1)–N(7) [2.187(4) Å], while when the hydrogen bonds between the two undeprotonated nitrogen atoms of the imidazole groups [N(2) and N(2a)] are the same in strength the two Cu$^{\text{II}}$–N$_{\text{imidazole}}$ bond distances are identical [Cu(1)–N(1) = Cu(1)–N(1a) 2.114(4) Å]. As a result, Cu$^{\text{II}}$ adopts a square-pyramidal geometry in **1** but a trigonal-bipyramidal geometry in **2**. Hydrogen bonds to the imidazole group also greatly influence the geometry of the copper(II) ions in **3** and **4**. When the lattice water molecule is hydrogen-bonded to the undeprotonated imidazole group in **3** the Cu–N bond length in basal positions is 0.1 Å shorter than that in the apical position, whereas the lattice water molecule is not hydrogen-bonded to the undeprotonated imidazole group in **4**. The Cu–N bond length in the basal plane, especially Cu–N(5), is even longer than that at the apical position. As a result, in **3** Cu$^{\text{II}}$ adopts an elongated square-pyramidal geometry but in **4** a flattened square-pyramidal geometry. We attribute the hydrogen bond influence on the geometry of the central metal atoms to the enhancement in coordination ability of the imidazole nitrogen atoms. Of interest is that the hydrogen bonds to the

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1**–**4**

	1	2	3	4
Cu(1)–N(1)	2.032(4)	2.114(4)	2.047(3)	2.099(3)
Cu(1)–N(3)	2.000(4)	1.968(5)	2.034(3)	1.997(6)
Cu(1)–N(4)	2.032(4)	1.984(8)	2.029(2)	2.045(6)
Cu(1)–N(5)	1.964(4)		1.998(3)	2.160(2)
Cu(1)–N(7)	2.187(4)			
Cu(1)–N(1a)		2.114(4)		
Cu(1)–N(3a)		1.968(5)		
Cu(1)–N(6a)			2.180(3)	2.055(6)
Hydrogen bonds				
N(2)···X	2.939(8)	3.006(7)	2.735(4)	
[H···X]	[2.10]	[2.15]	[1.854]	
(Angles)	(154.8)	(175.4)	(165.7)	
	(X = O(14a))	(X = F(4))	(X = O(1w))	
	3.049(11)	2.970(7)		
	[2.19]	[2.38]		
	(158.6)	(125.7)		
	(X = O(13b))	(X = F(6))		
N(6)···X	2.965(7) [2.12]			
[H···X]	(156.3)			
(Angles)	(X = O(1w))			
	2.961(8)			
	[2.45]			
	(116.0)			
	(X = O(21))			
N(2a)···X		3.006(7)		
[H···X]		[2.15]		
(Angles)		(X = F(4a))		
		2.970(7)		
		[2.38]		
		(X = F(6a))		

undeprotonated imidazole group also influence the crystallization form. When this group forms a hydrogen bond with a lattice water molecule **3** crystallizes in the centrosymmetric space group, while **4** crystallizes in a chiral space group. Although the effects of intramolecular hydrogen bonds to axial lengths, as well as to basal ligands on the crystallization pathway have been well investigated,[28] in all cases, the hydrogen bonds act directly on the coordinated atoms. It has not been found that hydrogen bonds indirectly acting on coordinated atoms affect their crystallization pathway.

Conclusion

We have reported the synthesis and crystal structures of four copper(II) complexes with Schiff base ligands containing twin imidazole groups. Based on the crystal structure analyses, it can be concluded that, by influencing the coordination ability of the imidazole group, hydrogen bonds to the imidazole group in five-coordinated copper(II) complexes can affect their geometry and their crystallization pathway.

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