Self-Assembly of Bis(pyrrol-2-ylmethyleneamine) Ligands with Cu^{II} Controlled by Bridging [−$(CH_2)_n$−] Spacers and Weak Intermolecular C−H···Cu Hydrogen Bonding

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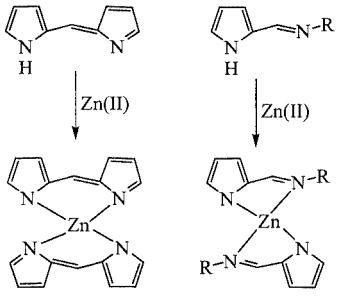
Keywords: Copper / Helical structures / Hydrogen bonding / N ligands / Schiff bases / Self-assembly

Bis(pyrrol-2-ylmetyhleneamine) ligands linked by alkyl spacers between the imine nitrogens are shown to give dinuclear dimers or mononuclear monomers, depending on the length of the alkyl linker, upon coordination with Cu^{II}. Ligands containing ethylene or hexylene linkers –$(CH_2)_n$– (n = 2, 6) give dinuclear dimers **5** and **8**, while propylene and butylene chains (n = 3, 4) give mononuclear monomers **6** and **7**. X-ray crystal structural analysis reveals that **5** exists as two very similar isomers **5a** and **5b**, in which the two ligands are bound to two Cu^{II} centers to form a distorted helical conformation. In the unit cells of **8**, two entirely different isomers **8a** and **8b** are found. In **8a** two ligands are side-by-side bound to two Cu^{II} centers to form a rectangular macrocycle, while in **8b** they are bonded to two Cu^{II} centers to form a distorted double-stranded helix. Moreover, X-ray structural analysis reveals that complexes **5**–**8** are further assembled into one-dimensional polymers through weak, intermolecular C–H···Cu hydrogen bonding, which plays a crucial role in stabilizing the crystal lattice.

Introduction

Metal-ion-assisted self-assembly is one of most powerful approaches to supramolecular architectures.[1] This strategy typically utilizes metal-ligand interactions to organize small molecules into large assemblies. Obviously the ligands are the key to such research. The dipyrrin ligands **I**, which are important synthetic precursors for porphyrins, bile pigments, and linear and cyclic polypyrroles,[2] were recently used for metal-ion-assisted self-assembly.[3,4] One of the advantages of using dipyrrins as a building block for self-assembly is their ability to form neutral complexes, meaning that counterions are not required, which makes it particularly convenient to purify the complexes by column chromatography since the complexes are not charged and are generally the least-polar component in the reaction mixtures.[3,4] This may also avoid the disordering problem in the solid state caused by counterions.



I Dipyrrin **II** Schiff-base Ligand

However, the use of dipyrrin for constructing supramolecular architectures by self-assembly is also limited by their availability and solubility in organic solvents. Spacer-bridged linear bis- or tris-dipyrrins are usually difficult to synthesize.[2,5] Moreover, linear poly(dipyrrin)s, such as tetradipyrrins, hexadipyrrins, have been reported to have limited solubility in common solvents.[5]

Having examined the chemical structure of dipyrrin **I**, we assumed that its simpler analogues **II** may possess similar coordinating properties to **I**, and may therefore be an ideal building block for supramolecular architectures. Ligands **II**, a pyrrol-2-yl Schiff base or pyrrol-2-ylmethyleneamine, could easily be prepared by condensation of 2-formylpyrrole with a primary amine. Complexes formed by **II** and

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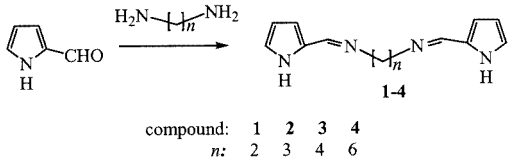
  DOI: 10.1002/ejic.200300639

metal ions have been known for a long time,[6] and macrocycles containing pyrrol-2-ylmethyleneamine units, such as texaphyrins and expanded porphyrins,[7] have been extensively investigated. Linear spaced bis(pyrrol-2-ylmethyleneamine) and their complexes with metal ions have been reported,[8] which shows that both the preparation of ligands and the complexes are highly efficient, and that the metal complexes formed by pyrrol-2-ylmethyleneamines possess good solubility in common solvents. Attracted by those properties, our group recently investigated the use of pyrrol-2-ylmethyleneamine ligands for self-assembly.[9−11] By varying the spacers between two pyrrol-2-ylmethyleneamine units, a two-dimensional network polymer,[9] dinuclear dimeric helicates,[10,11] trinuclear trimeric triangle[11] and tetranuclear tetrameric square[11] complexes were generated, which demonstrated that pyrrol-2-ylmethyleneamine ligands are ideal building blocks for self-assembly. Relative to its close analogues — pyridine-imine ligands[12] — the pyrrole-Schiff-base ligand can form neutral complexes, which allows a simpler purification and characterization. In this paper we report the self-assembly of bis(pyrrol-2-ylmethyleneamine) ligands controlled by the length of the bridging spacers and an "unconventional" weak intermolecular C−H···Cu hydrogen bonding, which is found in all the four copper complex crystals. This weak hydrogen bonding plays a crucial role in the architecture of the chain or 1D network polymers.

Results and Discussions

Structural Characterization

The bis(pyrrol-2-ylmethyleneamine) ligands **1**−**4** were synthesized in high yields by condensation of alkyl diamines with 2-formyl-1*H*-pyrroles in ethanol (Scheme 1). They are symmetrical in chemical structure, possess two Schiff-base units, and have good solubility in common solvents. Their structures were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry.



Scheme 1

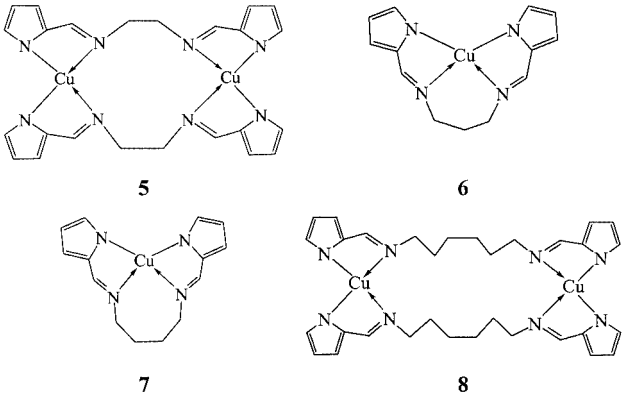
The Cu^{II} complexes **5**−**8** were prepared in yields of 55−75% by reaction of each of ligands **1**−**4** with Cu^{II} (Scheme 2). Complexes **5**−**7** possess good solubility in common solvents such as dichloromethane, chloroform, THF, and DMF, but are less soluble in methanol, ethanol, acetone, hexane, benzene, toluene and water. Complex **8** is insoluble in most solvents. Crystals of compounds **5**−**8** are

Table 1. Crystallographic data and structure refinement summary for complexes **5**−**8**

	5	**6**	**7**	**8v**
Formula	$C_{24}H_{24}Cu_2N_8$	$C_{13}H_{14}CuN_4$	$C_{14}H_{16}CuN_4$	$C_{32}H_{40}Cu_2N_8$
Molecular mass	551.59	289.82	303.85	666.82
Crystal system	triclinic	orthorhombic	monoclinic	triclinic
Space group	$P\bar{1}$	Pbca	$P2_1/c$	$P1$
a (Å)	41.183(11)	10.293(4)	10.1934(10)	11.8053(12)
b (Å)	20.154(6)	13.981(5)	13.0476(18)	12.5048(11)
c (Å)	8.689(3)	17.615(7)	11.2974(14)	12.5727(8)
α (°)	90	90	90	106.186(5)
β (°)	90	90	113.525(5)	104.138(3)
γ (°)	90	90	90	110.336(2)
$D_{calcd.}$ (g cm^{-3})	1.524	1.519	1.465	1.425
Volume (Å^3)	7212(4)	2535.0(17)	1377.7(3)	1546.8(2)
Z	12	8	4	2
Absorption coefficient (mm^{-1})	1.798	1.709	1.576	1.411
F(000)	3384	1192	628	692
Crystal size (mm^3)	0.30 × 0.10 × 0.06	0.24 × 0.20 × 0.08	0.52 × 0.18 × 0.11	0.62 × 0.16 × 0.12
h	−49/49	−12/7	−13/13	−15/15
k	−23/20	−12/16	−16/16	−16/16
l	−10/8	−18/20	−14/14	−17/17
Theta range (°)	1.98/25.03	2.31/25.00	2.68/27.48	1.99/27.48
Total reflections	28087	8186	5807	10375
Independent reflections	6332	2201	3132	10375
parameters	460	164	172	759
R[a]	0.0708	0.0664	0.0360	0.0483
wR [b]	0.1173	0.1043	0.0666	0.1005
Goodness of fit	1.010	0.975	0.634	0.813
Largest diff. Peak and hole (e·Å^{-3})	0.514/−0.465	0.532/−0.421	0.275/−0.501	0.714/−0.616

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

stable for several months under cold and dark conditions. Their solutions in dichloromethane or chloroform were found to slowly decompose upon exposure to light and air.



5 **6** **7** **8**

Scheme 2

Mass spectrometry was found to be especially informative in identifying the above reaction products. Analysis of the complexes, primarily by MALDI-TOF mass spectrometry, revealed that the molecular ions (*m*/*z*) observed in the mass spectra of **5** and **8** are 628 [M^+ + Cu] and 663 [M^+ + H], respectively, which were therefore assigned as dimeric complexes with a ligand:metal ratio of 2:2, while those of **6** and **7** are 289 [M^+] and 303 [M^+], respectively, which were assigned to the corresponding mononuclear monomeric complexes.

Crystal Structures

Crystals of **5**−**7** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/MeOH, whereas single crystals of **8** were prepared by layering a solution of $Cu(OAc)_2$ in CH_3OH upon a solution of **4** in $CHCl_3$ in a sealed tube with very careful diffusion. A summary of the crystal data of complexes **5**−**8** is given in Table 1.

By varying the length of the bridging −$(CH)_n$− spacer between the pyrrol-2-ylmethyleneamine units, self-assembly of bis(pyrrol-2-ylmethyleneamine) alkane ligands with Cu^{II} could offer mononuclear monomeric or dinuclear dimeric complexes. When n = 2, the self-assembly products are two very similar dinuclear dimeric complexes **5a** and **5b**, while in the case of n = 3 and 4, the products are the mononuclear monomeric complexes **6** and **7**, respectively, due to the greater flexibility of the spacer between the pyrrol-2-ylmethyleneamine units, which allows ligands **2** or **3** to coordinate to the same metal center. The tension of the shorter chain in ligand **1** makes it more likely to form a dinuclear dimeric complex. When n = 6, the complexation gives two

Table 2. Selected bond lengths for complex **5**−**8**

	Covalent bond lengths (Å)		Dative bond lengths (Å)	
5a	Cu(1)−N(1)	1.960(6)	Cu(1)−N(2)	2.006(6)
	Cu(1)−N(3)	1.947(6)	Cu(1)−N(4)	1.978(6)
	Cu(2)−N(5)	1.924(6)	Cu(2)−N(6)	1.983(6)
	Cu(2)−N(7)	1.947(7)	Cu(2)−N(8)	1.997(6)
5b	Cu(3)−N(9)	1.931(6)	Cu(3)−N(10)	1.973(6)
	Cu(3)−N(11)	1.963(6)	Cu(3)−N(12)	2.003(6)
6	Cu(1)−N(1)	1.944(7)	Cu(1)−N(2)	1.976(6)
	Cu(1)−N(4)	1.951(6)	Cu(1)−N(3)	1.984(6)
7	Cu−N(1)	1.959(3)	Cu−N(2)	2.005(2)
	Cu−N(4)	1.954(3)	Cu−N(3)	2.025(3)
8a	Cu(1)−N(1)	1.943(9)	Cu(1)−N(2)	2.028(9)
	Cu(1)−N(8)	1.981(9)	Cu(1)−N(7)	2.003(8)
	Cu(2)−N(4)	1.910(10)	Cu(2)−N(3)	1.934(10)
	Cu(2)−N(5)	1.940(12)	Cu(2)−N(6)	1.966(11)
8b	Cu(3)−N(9)	1.967(11)	Cu(3)−N(15)	1.979(6)
	Cu(3)−N(16)	1.945(8)	Cu(3)−N(10)	2.083(7)
	Cu(4)−N(12)	1.945(8)	Cu(4)−N(11)	2.045(6)
	Cu(4)−N(13)	1.980(8)	Cu(4)−N(14)	1.968(6)

Table 3. Selected bond angles (°) for **5**−**8**

5a			
N(3)−Cu(1)−N(1)	154.2(3)	N(5)−Cu(2)−N(7)	155.5(2)
N(3)−Cu(1)−N(4)	83.7(3)	N(5)−Cu(2)−N(6)	83.6(3)
N(1)−Cu(1)−N(4)	100.2(3)	N(7)−Cu(2)−N(6)	101.1(3)
N(3)−Cu(1)−N(2)	101.6(3)	N(5)−Cu(2)−N(8)	101.8(3)
N(1)−Cu(1)−N(2)	82.7(3)	N(7)−Cu(2)−N(8)	82.8(3)
N(4)−Cu(1)−N(2)	161.8(3)	N(6)−Cu(2)−N(8)	158.3(2)
5b			
N(9)−Cu(3)−N(11)	152.4(2)	N(9)−Cu(3)−N(12)	102.3(3)
N(9)−Cu(3)−N(10)	83.4(3)	N(11)−Cu(3)−N(12)	82.9(3)
N(11)−Cu(3)−N(10)	100.6(3)	N(10)−Cu(3)−N(12)	160.9(3)
6			
N(1)−Cu(1)−N(4)	101.9(3)	N(1)−Cu(1)−N(3)	166.9(2)
N(1)−Cu(1)−N(2)	82.6(3)	N(4)−Cu(1)−N(3)	82.5(3)
N(4)−Cu(1)−N(2)	175.3(3)	N(2)−Cu(1)−N(3)	92.7(3)
7			
N(4)−Cu−N(1)	100.45(11)	N(4)−Cu−N(3)	82.96(11)
N(4)−Cu−N(2)	160.71(10)	N(1)−Cu−N(3)	170.46(11)
N(1)−Cu−N(2)	83.19(11)	N(2)−Cu−N(3)	96.55(11)
8a			
N(1)−Cu(1)−N(8)	155.6(3)	N(4)−Cu(2)−N(3)	83.7(5)
N(1)−Cu(1)−N(7)	100.1(3)	N(4)−Cu(2)−N(5)	154.5(4)
N(8)−Cu(1)−N(7)	83.0(3)	N(3)−Cu(2)−N(5)	99.4(5)
N(8)−Cu(1)−N(2)	103.8(3)	N(4)−Cu(2)−N(6)	103.8(5)
N(8)−Cu(1)−N(2)	103.8(3)	N(3)−Cu(2)−N(6)	157.3(4)
N(7)−Cu(1)−N(2)	156.3(3)	N(5)−Cu(2)−N(6)	83.1(5)
8b			
N(16)−Cu(3)−N(9)	166.0(4)	N(12)−Cu(4)−N(13)	162.8(3)
N(16)−Cu(3)−N(15)	85.0(3)	N(12)−Cu(4)−N(14)	103.5(3)
N(9)−Cu(3)−N(15)	98.4(3)	N(13)−Cu(4)−N(14)	84.4(2)
N(16)−Cu(3)−N(10)	98.2(3)	N(12)−Cu(4)−N(11)	80.2(3)
N(9)−Cu(3)−N(10)	81.8(3)	N(13)−Cu(4)−N(11)	97.5(2)
N(15)−Cu(3)−N(10)	166.2(2)	N(14)−Cu(4)−N(11)	160.7(2)

Table 4. The dihedral angles between two Cu−N−N terminal planes

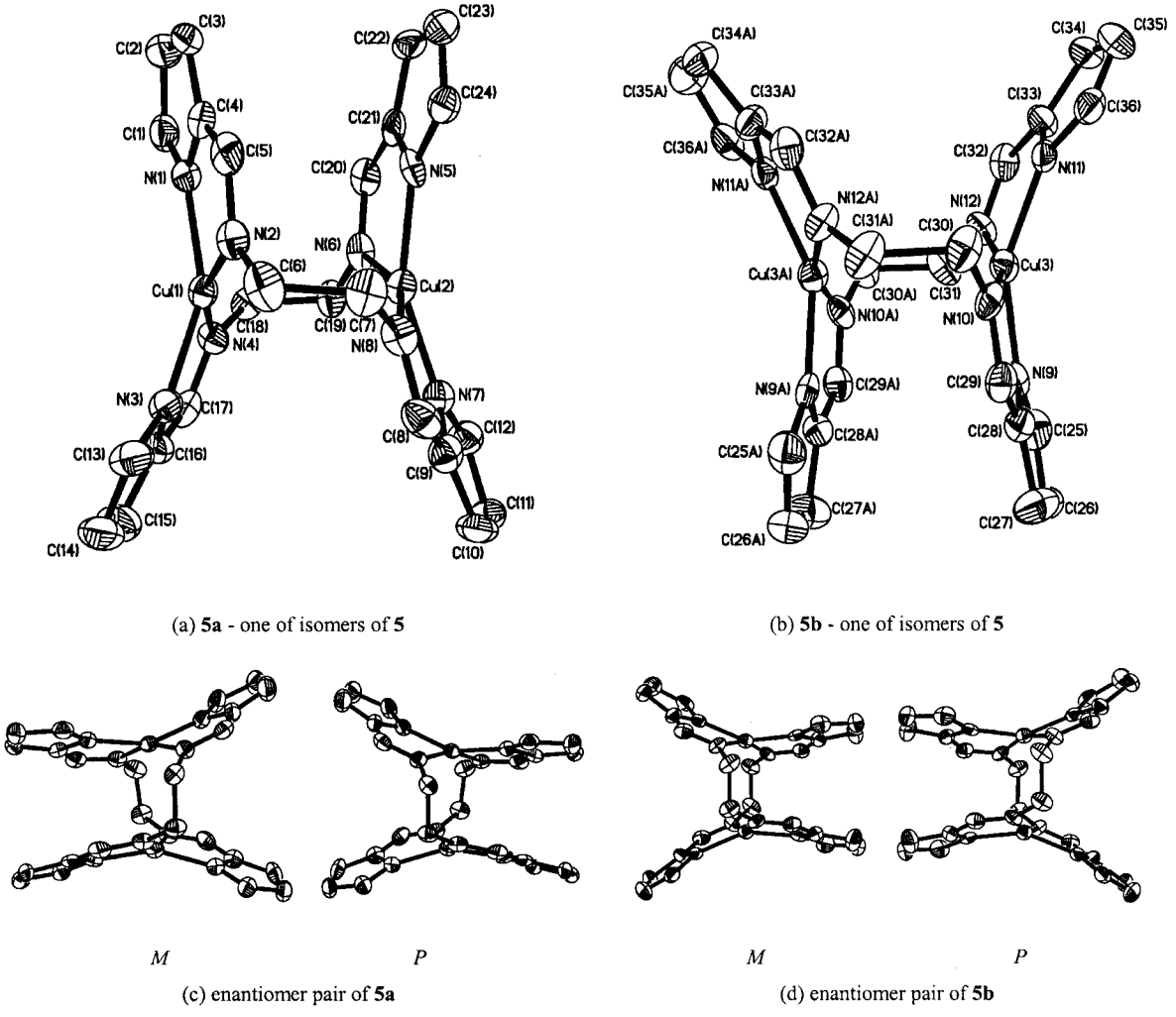
	5a	5b	6	7	8a	8b
Dihedral angles (°)	33.8 (Cu1) 35.1 (Cu2)	36.9 (Cu3) 36.9 (Cu4)	12.3	22.6	37.4 (Cu1) 35.3 (Cu2)	20.6 (Cu3) 27.3 (Cu4)

dinuclear dimeric isomers — a side-by-side conformer (**8a**) and helical conformer (**8b**) — thus avoiding the steric crowding of six CH_2 groups constrained in a relatively small space which would be the case for a mononuclear monomer conformation. The crystallographic data show that the tetrahedral sp^3 angles in the spacers of all complexes are close to 109.5°, which also suggests that the dinuclear dimeric complexes **5** and **8** and mononuclear monomeric complexes **6** and **7** are stable species.

The Cu^{II} centers have a distorted square-planar geometry for complexes **5**−**8**. Each Cu^{II} center is tetracoordinate to four N atoms from two pyrrol-2-ylmethyleneamine units. The covalent Cu−N distance is in the range of 1.910−1.981 Å, while the dative Cu−N separation is between 1.940 and 2.083 Å. These distances are similar to the length range of Cu−N bonds found in the literature.[13] Selected bond lengths and angles for complexes **5**−**8** are shown in Table 2 and Table 3, respectively.

The dihedral angles, which are defined by the intersection of two pyrrol-2-ylmethyleneamine planes at the copper center, are in the range of 12.3−37.4°, indicating that the copper centers of complex **6** have the smallest deviation from the square-planar coordination geometry (see Table 4).

In the crystal of complex **5**, it was found that the unit cell contains two different isomers, **5a** and **5b**, both of which adopt a double-stranded helical conformation[13a,14] (Figure 1). However, **5b** has D_2 symmetry while **5a** has C_2 sym-



(a) **5a** - one of isomers of **5**

(b) **5b** - one of isomers of **5**

(c) enantiomer pair of **5a**

(d) enantiomer pair of **5b**

Figure 1. ORTEP views of complex **5** (30% thermal probability ellipsoids) with atom numbering; protons are omitted for clarity: (a) **5a**; (b) **5b**; (c) *M* and *P* helical enantiomers of **5a**; (d) *M* and *P* helical enantiomers of **5b**

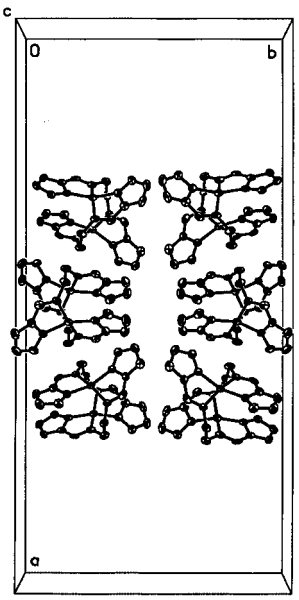


Figure 2. The enantiomer pairs of **5a** and **5b** arranged in the crystal; protons are omitted for clarity

metry. In addition, the torsion angles of the N(imine)−CH_2−CH_2−N(imine) groups in **5a** is −58.4° (N4−C18−C19−N6) and −56.8° (N2−C6−C7−N8) while the corresponding angle in **5b** is −61.8°.

In both **5a** and **5b**, two pyrrol-2-ylmethyleneamine units of the same ligand are found to adopt a *cis* arrangement, which is different from the *trans* arrangement of the Zn^{II} analogue and other bis(pyrrol-2-ylmethyleneamine)zinc(II) complexes.[9−11] This may be due to the geometry requirement of the different metal centers. The Cu···Cu distances are 3.242 Å and 3.257 Å for **5a** and **5b**, respectively. Interestingly, the *M* and *P* helical enantiomers of **5a** and **5b** are found in the crystal (see c and d in Figure 1) and they are arranged alternately (Figure 2).

Unlike complex **5**, complexes **6** and **7** are mononuclear complexes and each ligand uses all its N atoms to bind to the same metal center. The structures of complex **6** and **7** are very similar. However, the dihedral angles between the two Cu−N−N terminal planes are 12.3° and 22.6° for **6** and **7**, respectively, indicating that the Cu center in complex **6** is closer to an ideal square-planar geometry (Figure 3 and 4). Like complex **5**, *M* and *P* helical enantiomers are found for complexes **6** and **7** (Figure 3 and 4).

Interestingly, two different molecules (**8a**, **8b**) were found in the unit cell of complex **8**, which is similar to Dietrich-Buchecker's observations[15b] in solution. In **8a**, two pyrrol-2-ylmethyleneamine units in the same ligand adopt a *cis* arrangement along the hexylene chain (Figure 5). Two ligands are bound parallel to two copper centers to form an 18-membered rectangular macrocycle with cavity dimensions of approximately 7.7 × 3.9 Å. In **8b**, two pyrrol-2-ylmethyleneamine groups in the same ligand adopt a *trans* arrangement along the hexylene bridging chain, forming a distorted double-stranded helical configuration. As a result, this pattern of self-assembly also gives an 18-membered, distorted square-shaped macrocycle with cavity dimensions of approximately 6.4 × 6.1 Å.

The Cu···Cu distances are 8.405 Å for **8a** and 7.744 Å for **8b**, which are much longer than the corresponding distances

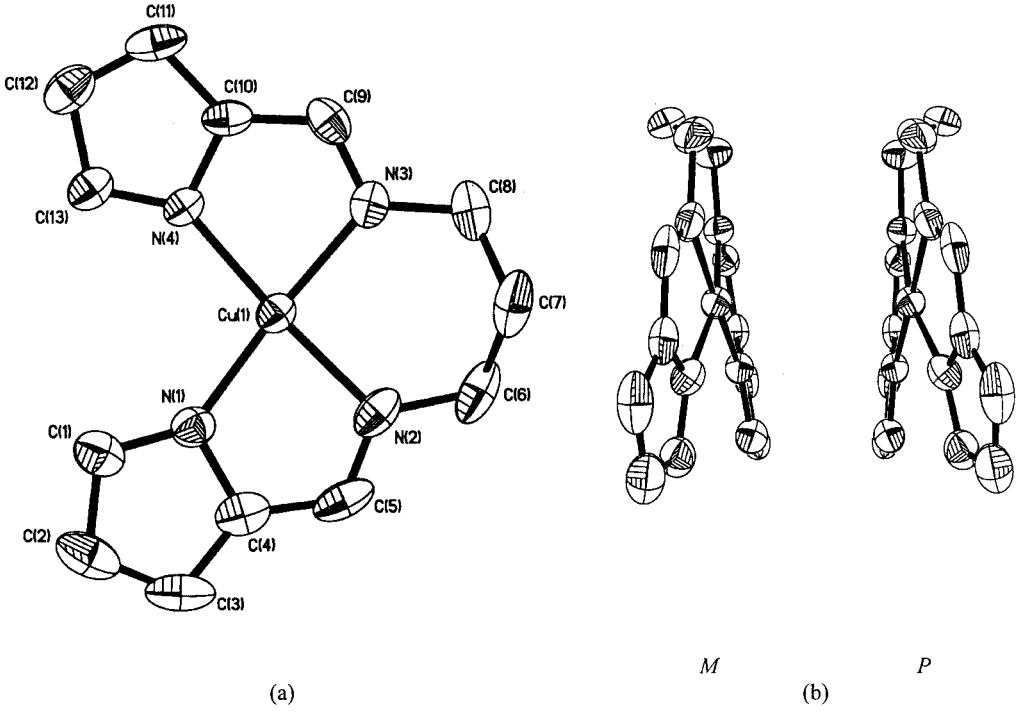


Figure 3. ORTEP views (30% thermal probability; protons are omitted for clarity) of: (a) complex **6**; (b) *M* and *P* helical enantiomers of **6**

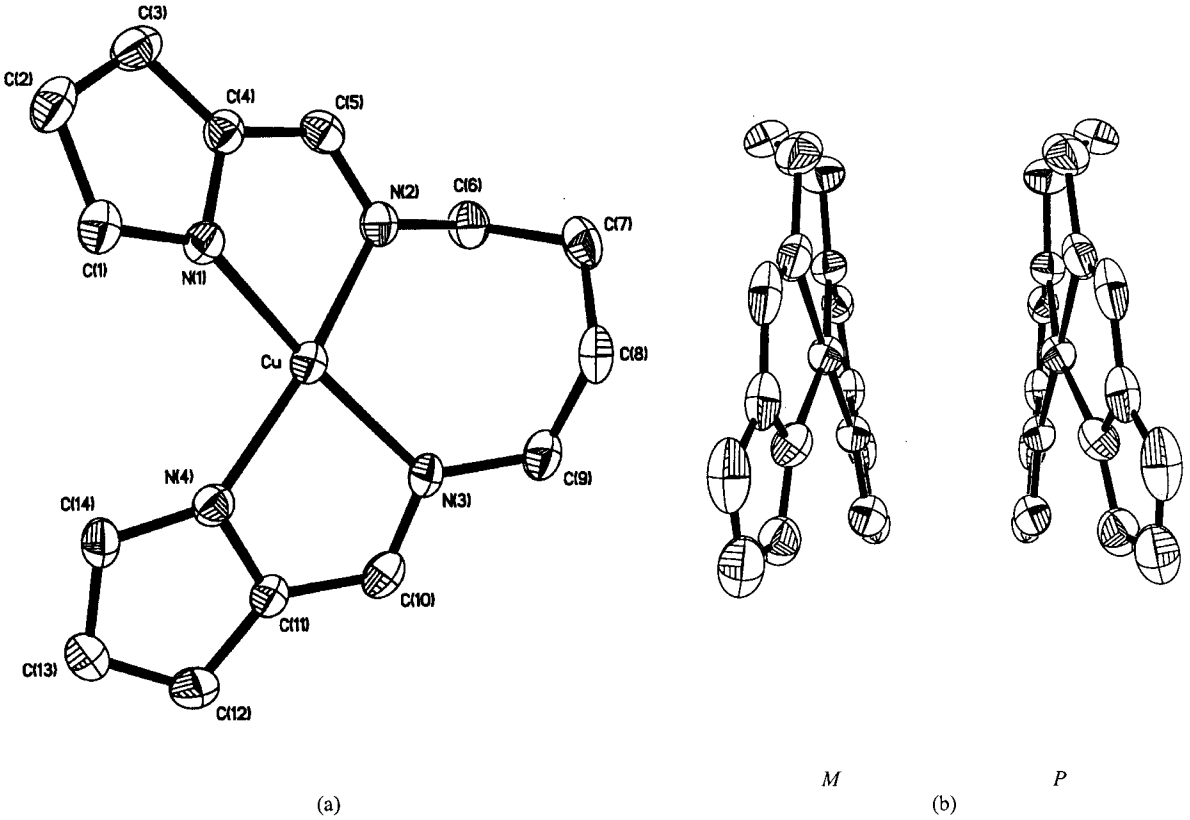


Figure 4. ORTEP view (30% thermal probability; protons are omitted for clarity) of: (a) complex **7**; (b) *M* and *P* helical enantiomers of **7**

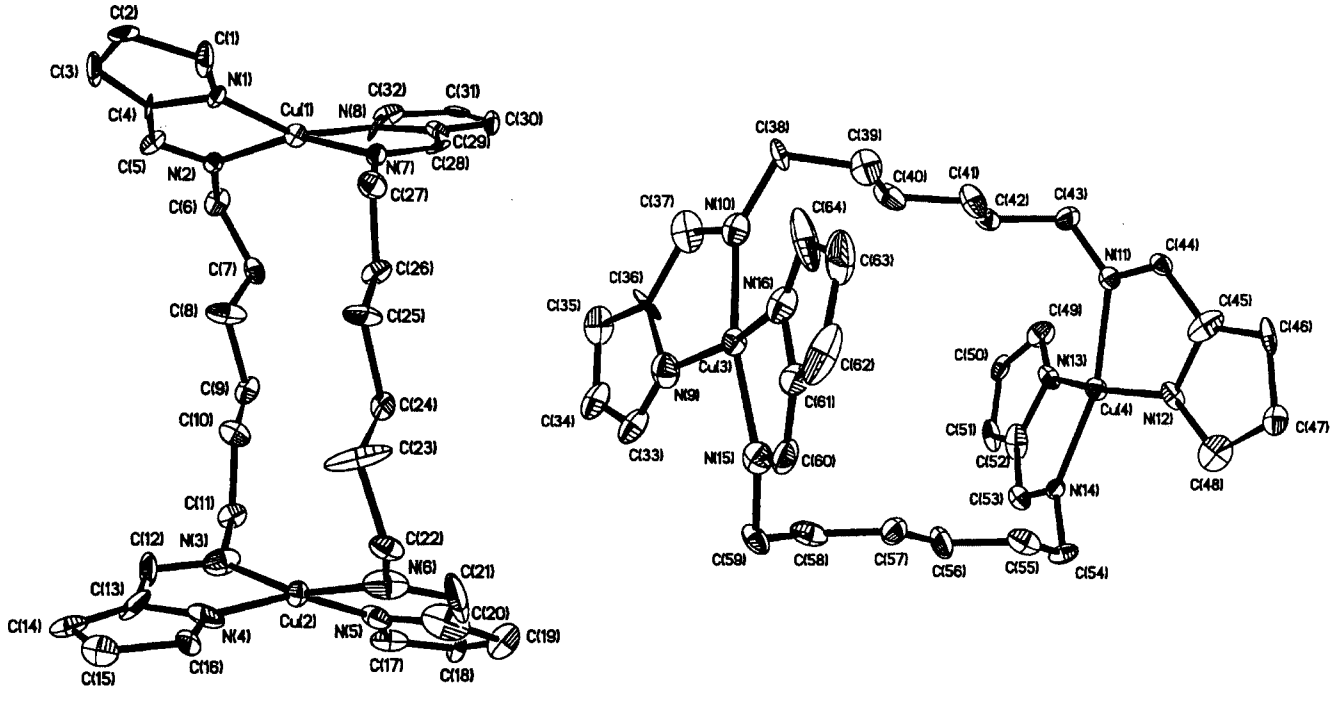


Figure 5. ORTEP view of complex **8** (30% thermal probability, protons are omitted for clarity) of: (a) **8a** (the C_{2h}-side-by-side conformer) and (b) **8b** (the *D_2-helical conformer)*

in complex **5** due to the longer spacer of the ligand in complex **8**. In **8a**, the dihedral angles at the Cu centers are 37.4° [Cu(1)] and 35.3° [Cu(2)], which are very close to the value for complex **5**, but larger than that in **8b** (Table 4). Unlike complexes **5**−**7**, there is no enantiomer pair found in the crystal of complex **8**.

Weak Hydrogen Bonding

Weak hydrogen bonding has been known to play a crucial role in chemical and biological systems.[15] Interestingly, the crystallographic characterization suggests that the Cu^{II} centers in complexes **5**−**8** participate in weak hydrogen bonding, which plays a crucial role in the formation of chain-type polymers or 1D networks. Although regular weak hydrogen bonding is very common,[16] weak hydrogen bonding with Cu^{II} is rare.[16b] However, copper is an electron-rich metal atom with filled *d*-orbitals that is capable of forming hydrogen bonds with a suitable donor to form a three-center, four-electron interaction (3*c*-4*e*).[16b,16c,16f] In complexes **5**−**8**, the H···Cu separation (d) is in the range of 2.804−3.018 Å, the C−H···Cu separation (D) is in the range of 3.637−3.921 Å and the C−H···Cu angle (θ) is between 84.9 and 168.0° (Table 5), which are similar to the values for weak hydrogen bonding found in the literature.

In complex **5**, a hydrogen atom from the CH_2 group in one molecule is bound to the Cu^{II} center of the second molecule (Figure 6, a). As a result, a triple-row 1D network is formed though weak C−H···Cu interactions with a row of **5a** on each side and **5b** in the middle (see b and c in Figure 6).

Unlike complex **5**, in complexes **6** and **7** the hydrogen atom at the 3-position of the pyrrole ring in one molecule is bound to the Cu^{II} center of the second molecule to form 1D extended chains (Figure 7). Interestingly, in the packing diagram of **6**, the *M* and *P* isomers are arranged in alternating rows when viewed along the *c* axis (Figure 7, a). However, in the packing diagram of **7** the *M* and *P* enantiomers are arranged alternately in the same chain (Figure 7, b). The Cu···H distances (d), C−H···Cu distance (D) and C−H···Cu angles (θ) are 3.018 Å, 3.637 Å and 84.9°, respectively, for **6**, and 2.842 Å, 3.637 Å and 144.1°, respectively, for **7**, indicating a stronger interaction in **7** than in **6**.

Table 5. Parameters for C−H···Cu intermolecular hydrogen bonding in complexes **5**−**8**

	d (Å)	*D* (Å)	θ(C−H···Cu) (°)
5	2.993[a]	3.671[a]	133.7[a]
	2.804[b]	3.758[b]	168.0[b]
6	3.018	3.637	84.9
7	2.842	3.637	144.1
8	2.998[c]	3.921[c]	159.4[c]
	2.941[d]	3.739[d]	140.3[d]

[a] For C(6A)−H(6A)···Cu(3A). [b] For C(30B)−H(30B)···Cu(1B). [c] For C(43A)−H(43A)···Cu(1A). [d] For C(58B)−H(58B)···Cu(2B).

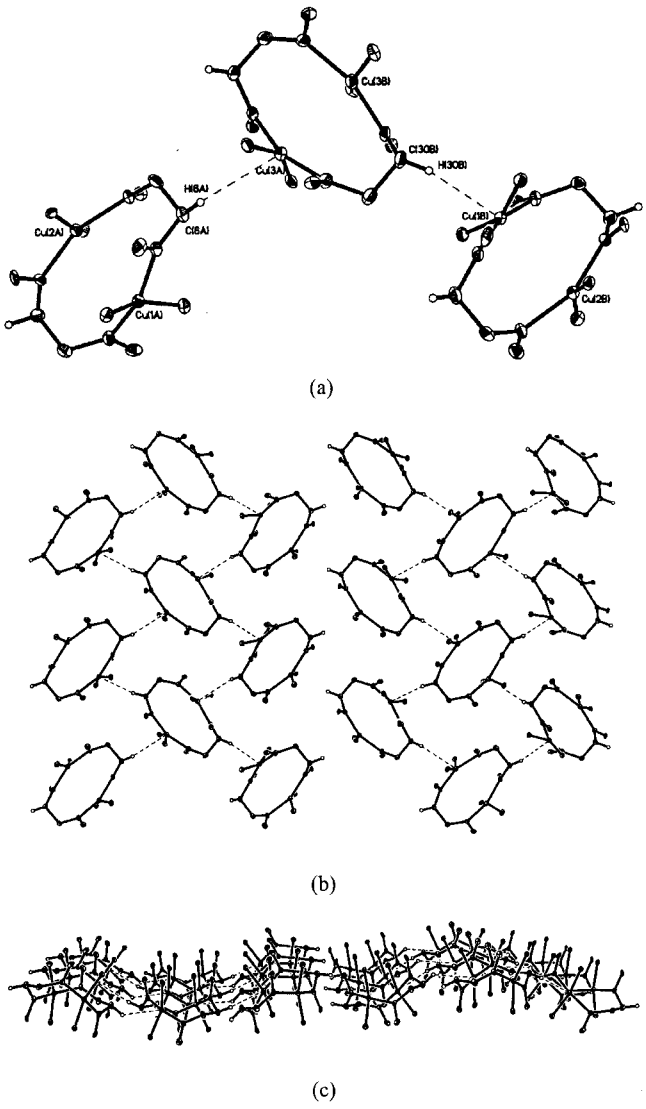


Figure 6. Weak hydrogen bonding in complex **5**; carbon atoms of the pyrrole ring are omitted for clarity: (a) weak C−H···Cu hydrogen bonding between **5a**−**5b**−**5a**; (b) view of triple-row 1D network along the *b* axis; (c) view of the triple-row 1D network along the *c* axis

Like complex **5**, one H atom of the CH_2 group in the bridge of each ligand is weakly bound to the Cu^{II} center from another molecule to form a 1D chain for complex **8**. However, unlike the interaction pattern in **5**, in which each molecule offers a hydrogen donor and a Cu^{II} acceptor to form the 1D networks, and also unlike the interaction pattern in **6** and **7**, in which each molecule acts as both acceptor and donor to form 1D chains, in complex **8** each helical conformer (**8b**) offers two hydrogen atoms from two different ligands and binds to two Cu^{II} centers of two side-by-side conformers (**8a**; Figure 8). In other words, **8b** acts only as a donor and **8a** acts only as an acceptor.

In conclusion, the self-assembly of bis(pyrrol-2-ylmethyleneamine) ligands with Cu^{II} gives mononuclear monomeric complexes or dinuclear dimeric complexes depending on the bridging spacer between the two pyrrol-2-ylmethyleneamine units. In all cases, the metal centers are four-coordinate with

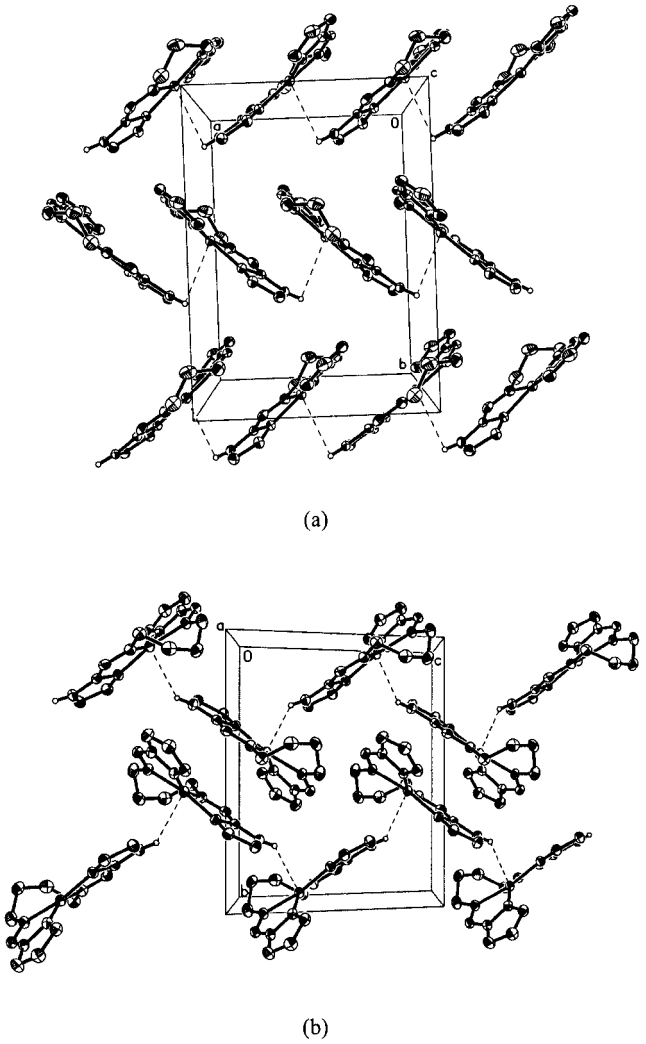


Figure 7. 1D chains formed through weak hydrogen bonding in complexes **6** and **7**: (a) one enantiomer of complex **6** in each row is ordered parallel through weak C−H···Cu hydrogen bonding, and the rows are arranged in a zigzag pattern; (b) 1D chains constructed through weak C−H···Cu hydrogen bonding in **7**

a distorted planar conformation. Moreover, the bis(pyrrol-2-ylmethyleneamine) ligands are doubly deprotonated, which allows the formation of neutral complexes in high yields. By varying the length of the bridging $-(CH)_n-$ spacer between the pyrrol-2-ylmethyleneamine units, self-assembly of bis(pyrrol-2-ylmethyleneamine)alkane ligands with Cu^{II} could offer mononuclear monomeric or dinuclear dimeric complexes. The self-assembly, which changes with the bridging spacers, reflects the steric requirement of the complexation. Intermolecular weak C−H···Cu hydrogen bonding is found in all complexes **5**−**8** and plays a major role in constructing 1D chains or network polymers.

In light of the high yields of the neutral complexes, their excellent solubility, the easy synthesis of the ligands and their great flexibility to generate supramolecules with interesting geometric structures, pyrrol-2-ylmethyleneamine has been demonstrated to be an ideal building block for supramolecular architectures through self-assembly. Our future work will be focused on the design, synthesis and self-assembly of ligands containing multiple pyrrol-2-ylmethyleneamine units.

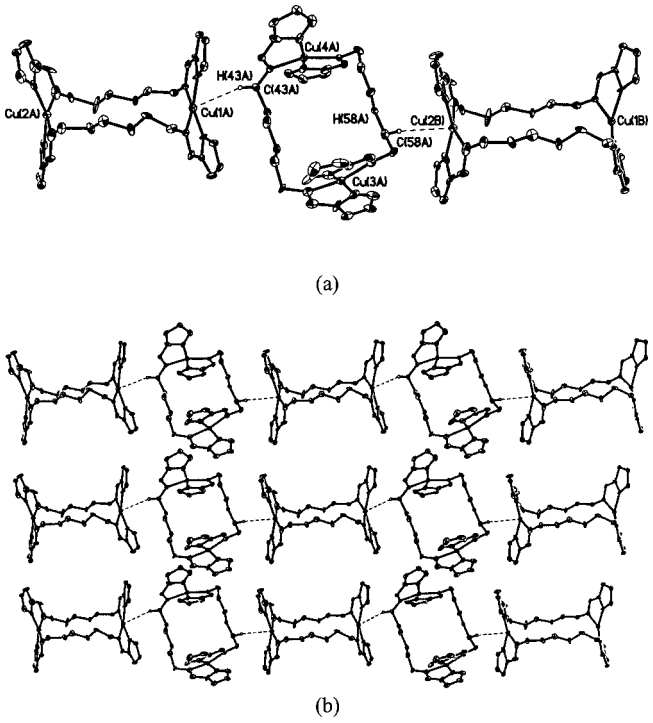


Figure 8. (a) 1D chain constructed by weak intermolecular hydrogen bonding in **8**; isomers **8a** and **8b** are arranged alternately; (b) the packing diagram of **8** showing the 1D chains

Experimental Section

All reagents for syntheses and analyses were of analytical grade and used as received. Melting points were determined on a Yanaco MP-500 micro-melting point apparatus. NMR spectra were recorded on a Bruker Avance dpx 400 MHz instrument using TMS as internal standard. Mass spectra were obtained on Bruker APEX II and KYKY-ZHP-5 spectrometers. IR spectra were recorded on a BIO-RAD FT-165 IR spectrometer. Elemental analyses were performed on a Carlo Erba-120 elemental analyzer.

General Procedure for the Synthesis of Ligands 1−4: Pyrrol-2-carbaldehyde (1.9 g, 20 mmol) and the linear diaminoalkane (10 mmol) were dissolved in ethanol (20 mL). The mixture was stirred for a while and then a few drops of glacial acetic acid were added. After a few seconds a white precipitate was observed. The suspension was stirred at room temperature for 2 h. The white solid was collected by suction filtration, washed with cold ethanol and dried under vacuum to give the expected product. The analytic sample was purified by re-crystallization from ethanol.

1,2-Bis(pyrrol-2-ylmethyleneamine)ethane (1): Yield: 1.61 g, 75%; m.p. 178−181 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 3.78 (s, 4 H, CH_2), 6.23 (dd, J = 3.5, 3.5 Hz, 2 H, pyrrole-H), 6.47 (dd, J = 3.5, 1.3 Hz, 2 H, pyrrole-H), 6.89 (m, 2 H, pyrrole-H), 8.04 (s, 2 H, imine-H) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = 61.4, 109.8, 114.5, 122.0, 130.1, 152.8 ppm. FAB-MS: *m*/*z* (%) =215 (30) [M^+ + H]. FT-IR (KBr pellet): $\tilde{\nu}$ = 3178, 3088, 2974, 2943, 2870, 1641, 1424, 1317, 1130, 1048, 1014, 828, 736 cm^{-1}.

1,3-Bis(pyrrol-2-ylmethyleneamine)propane (2): Yield: 1.44 g, 65%; m.p. 119−120 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.96 (t, *J* = 7.0 Hz, 2 H, CH_2), 3.58 (t, *J* = 7.0 Hz, 4 H, CH_2), 6.21 (t, *J* = 3.2 Hz, 2 H, pyrrole-H), 6.45 (d, *J* = 3.2 Hz, 2 H, pyrrole-H), 6.86 (m, 2 H, pyrrole-H), 8.01 (s, 2 H, imine-H) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = 32.7, 58.3, 109.7, 114.2, 121.9, 130.4, 152.1 ppm. FAB-MS: *m*/*z* (%) = 229 (30) [M^+ + H]. FT-IR (KBr pellet): ν̃ = 3117, 3062, 2966, 2943, 2850, 1637, 1445, 1420, 1314, 1131, 1097, 1033, 989, 750 cm^{-1}.

1,4-Bis(pyrrol-2-ylmethyleneamine)butane (3): Yield: 1.89 g, 78%; m.p. 178−179 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.73 (m, 4 H, CH_2), 3.55 (t, *J* = 3.8 Hz, 4 H, CH_2), 6.25 (dd, *J* = 3.4, 3.2 Hz, 2 H, pyrrole-H), 6.52 (dd, *J* = 3.4, 1.0 Hz, 2 H, pyrrole-H), 6.94 (m, 2 H, pyrrole-H), 7.99 (s, 2 H, imine-H) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = 28.7, 59.8, 110.2, 115.3, 122.9, 129.7, 151.6 ppm. FAB-MS: *m*/*z* (%) = 243 (70) [M^+ + H]. FT-IR (KBr pellet): ν̃ = 3164, 2970, 2928, 2897, 2848, 1644, 1424, 1360, 1136, 1099, 1035, 995, 829, 728 cm^{-1}.

1,6-Bis(pyrrol-2-ylmethyleneamine)hexane (4): Yield: 2.16 g, 80%; m.p. 131−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.36 (m, 4 H, CH_2), 1.61 (m, 4 H, CH_2), 3.50 (t, *J* = 6.7 Hz, 4 H, CH_2), 6.22 (t, *J* = 2.9 Hz, 2 H, pyrrole-H), 6.47 (dd, *J* = 2.9, 1.3 Hz, 2 H, pyrrole-H), 6.86 (m, 2 H, pyrrole-H), 8.03 (s, 2 H, imine-H) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = 27.1, 31.3, 60.7, 109.5, 114.2, 122.0, 130.4, 152.1 ppm. FAB-MS: *m*/*z* (%) = 271 (30) [M^+ + H]. FT-IR (KBr pellet): ν̃ = 3166, 3096, 2972, 2932, 2899, 2851, 1646, 1424, 1367, 1319, 1362, 1098, 1019, 959, 830, 728, 605cm^{-1}.

General Procedure for the Synthesis of 5−7: A solution of $Cu(OAc)_2{\cdot}H_2O$ (0.2 g, 1 mmol) in methanol (20 mL) was added to a solution of ligand (**1**−**3**, 1 mmol) in methanol (10 mL). A yellow-green precipitate appeared quickly. After 1.5 h the precipitates were collected by suction filtration and washed with methanol. Crystals suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/CH_3OH with a yield of 65−75%.

Cu^{II} Complex of 1,2-Bis(pyrrol-2-ylmethyleneamine)ethane (5): Yield: 193 mg, 70%; m.p. > 210 °C (decomp.). IR (KBr pellet): ν̃ = 3442, 3093, 2905, 1587, 1443, 1391, 1345, 1309, 1035, 738 cm^{-1}. MALDI-TOF-MS: 628 *m*/*z* = [M^+ + Cu]. $C_{24}H_{24}Cu_2N_8$ (551.59): calcd. C 52.26, H 4.39, N 20.31; found C 52.36, H 4.41, N 19.99.

Cu^{II} Complex of 1,3-Bis(pyrrol-2-ylmethyleneamine)propane (6): Yield: 188 mg, 65%; m.p. > 185 °C (decomp.). IR (KBr pellet): ν̃ = 3444, 3089, 2900, 2838, 1600, 1514, 1439, 1395, 1033, 735 cm^{-1}. MALDI-TOF-MS: *m*/*z* = 289 [M^+]. $C_{13}H_{14}CuN_4$ (289.82): calcd. C 53.87, H 4.87, N 19.33; found C 53.65, H 4.85, N 19.08.

Cu^{II} Complex of 1,4-Bis(pyrrol-2-ylmethyleneamine)butane (7): Yield: 227 mg, 75%; m.p. 160−161 °C. IR (KBr pellet): ν̃ = 3430, 3090, 2928, 2854, 1601, 1513, 1440, 1393, 1363, 1089, 1033, 744 cm^{-1}. MALDI-TOF-MS: *m*/*z* = 303 [M^+]. $C_{14}H_{16}CuN_4$ (303.85): calcd. C 55.34, H 5.31, N 18.44; found C 55.07, H 5.29, N 18.19.

Synthesis of Cu^{II} Complex of 1,6-Bis(pyrrol-2-ylmethyleneamine)-hexane (8): This complex was prepared by laying a solution of $Cu(OAc)_2{\cdot}H_2O$ (39 mg, 0.2 mmol) in CH_3OH (6 mL) on top of a solution of **4** (54 mg, 0.2 mmol) in $CHCl_3$ (8 mL) in a sealed tube. After several days, crystals of **8** suitable for X-ray analysis were obtained. Yield: 182 mg, 55%. m.p. > 250 °C (decomp.). FT-IR (KBr pellet): ν̃ = 3443, 3093, 2929, 2853, 1593, 1515, 1441, 1391, 1341, 1313, 1034, 740 cm^{-1}. MALDI-TOF-MS: *m*/*z* = 663 [M^+ + H]. $C_{32}H_{40}Cu_2N_8$ (663.81): calcd. C 57.90, H 6.07, N 16.88; found C 58.14, H 6.15, N 16.92.

X-ray Crystallography: Crystals suitable for X-ray diffraction studies were obtained as described above. Accurate unit cell parameters were determined by a least-squares fit of 2θ values, measured for 200 strong reflections, and intensity data sets were measured on a Bruker Smart 1000 CCD or Rigarku Raxis Rapid IP diffractometer with Mo-K_α radiation (λ = 0.71073 Å) at room temperature. The intensities were corrected for Lorentz and polarization effects, but no corrections for extinction were made. All structures were solved by direct methods. The non-hydrogen atoms were located in successive difference Fourier synthesis. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically and treated as riding on the concerned atoms. Crystallographic data and experimental details for structure analyses are summarized in Table 1.

CCDC-209047 ... -209050 (for **5**−**8**, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html. [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

This work was supported by the Major State Basic Research Development Program (G2000078100), NSFC (20172055) and CAS (CMS CX-200205). We thank Ms. S.-H. Zhou (Institute of Biophysics) for the NMR spectra and Dr. H. Liu for helpful discussions on crystal-structure analysis.

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Received September 10, 2003
Early View Article
Published Online February 26, 2004

