Self-Assembly of Pyrrole Derivatives

Double-Stranded Helicates, Triangles, and Squares Formed by the Self-Assembly of Pyrrol-2-ylmethyleneamines and Zn^{II} Ions**

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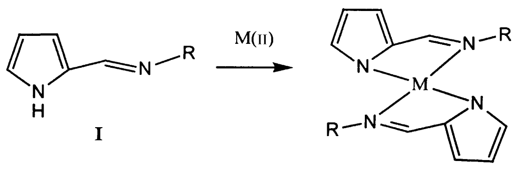
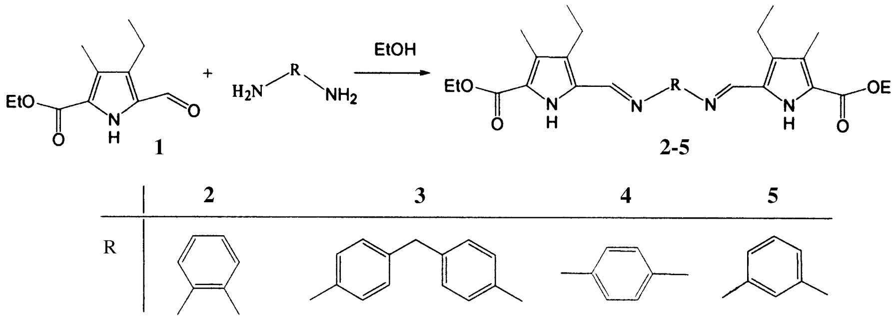
The metal complexes of ligands **I**, a pyrrol-2-yl Schiff base or pyrrol-2-ylmethyleneamine, have been known for a long time.[1–3] Macrocycles containing pyrrol-2-ylmethyleneamine units, such as texaphyrins and expanded porphyrins,[4] have been extensively investigated. Linear-spacer-bridged bis(pyrrol-2-ylmethyleneamine)s and their complexes with metal ions were recently reported,[5–9] which showed that both the preparation of the ligands and the complexes were highly efficient, and the metal complexes formed by pyrrol-2-ylmethyleneamines possessed good solubility in common solvents. These facts encouraged us to explore their use as a building block for supramolecular self-assembly. In this paper we report the neutral double-stranded helicates, trimeric triangles, and tetrameric squares formed through the self-assembly of spacer-bridged bis(pyrrol-2-ylmethyleneamine) ligands with Zn^{II} ions.



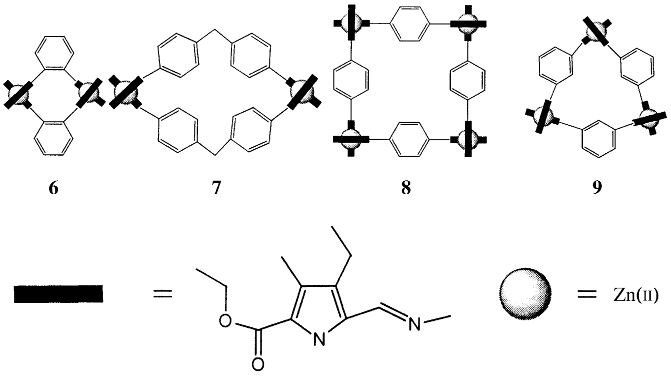
I

Ligands **2**–**5** were prepared in high yields (Scheme 1) by the condensation of diamines with 4-ethyl-5-formyl-3-methyl-1*H*-pyrrole-2-carboxylic acid ethyl ester (**1**) in ethanol. The ligands **2**–**5** were each reacted with zinc(II) acetate dihydrate in THF (Scheme 2), to give the complexes **6**–**9**, respectively, in excellent yields. The complexes, isolated as red (**6** and **8**) or yellow (**7** and **9**) powders, are soluble in most common organic solvents. Crystals were grown by slowly evaporating their solutions in THF/EtOH (**6** and **7**), THF/MeOH (**8**), or THF/di(ethylene glycol) (**9**). All of the crystals are stable in the dark under a nitrogen atmosphere, but decomposed quickly in the air.



Scheme 1. Synthesis and structure of ligands **2**–**5**.

Analysis of the complexes, primarily by MALDI-TOF mass spectrometry, showed that the molecular masses of **6** and **7** were 1105 and 1284, respectively, which corresponds to dimeric complexes with two ligands and two zinc centers. However, the molecular masses of **8** and **9** were found to be 2209 and 1675, which corresponds to a tetrameric complex (four ligands and Zn centers) and trimeric complex (three ligands and Zn centers), respectively.



Scheme 2. Schematic representation of complexes **6**–**9**.

The ^{1}H NMR spectra of the zinc complexes **6**–**9** in $CDCl_3$ show a single set of proton resonances that could be fully assigned, which suggests that they exist as single species in solution. In all cases, the disappearance of the NH protons from the free ligands was observed, which is in agreement

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with the double deprotonation of the Schiff bases. In comparison with the corresponding free ligands, complexes **6**–**9** have up-field shifts for most of the protons. Interestingly, the -CH$_2$- groups in both the ester group and pyrrole ring of complexes **6**, **8**, and **9**, in which there are rigid phenylene spacers, show chiral behavior in solution. In the free ligands, the two protons of the -CH$_2$- groups of the ethyl ester moieties are identical and give a single quartet, however, they appear as two sets of multiplets in the complexes. Similar behavior was observed for the methylene protons of the ethyl groups in pyrrole ring. These results imply that the strong coordination of the pyrrol-2-ylmethyleneamine with the zinc ion removes the inherent enantiotropic nature of the protons making them diastereotopic and chiral. These observations are very similar to those reported by Bermejo and coworkers.[9] The ^{13}C NMR spectra of complexes **6**–**9** in CDCl$_3$ consist of the expected signals.

X-ray analysis of complexes **6**[10] (Figure 1 a) and **7**[11] (Figure 1 b) indicate that their structures possess a double-stranded helical geometry that results from a severe twist around the phenyl or diphenylmethane bridge. This twist divides the ligand into two pyrrol-2-ylmethyleneamine subunits, each of which is bound to a different Zn^{II} ion. As a result, the Zn^{II} center and its two pyrrol-2-ylmethyleneamine segments have an almost tetrahedral geometry, from which the bond angles and bond lengths have only a small deviation. The two Zn^{II} ions in **6** and **7** are separated by 3.7 Å and 11.0 Å, respectively.

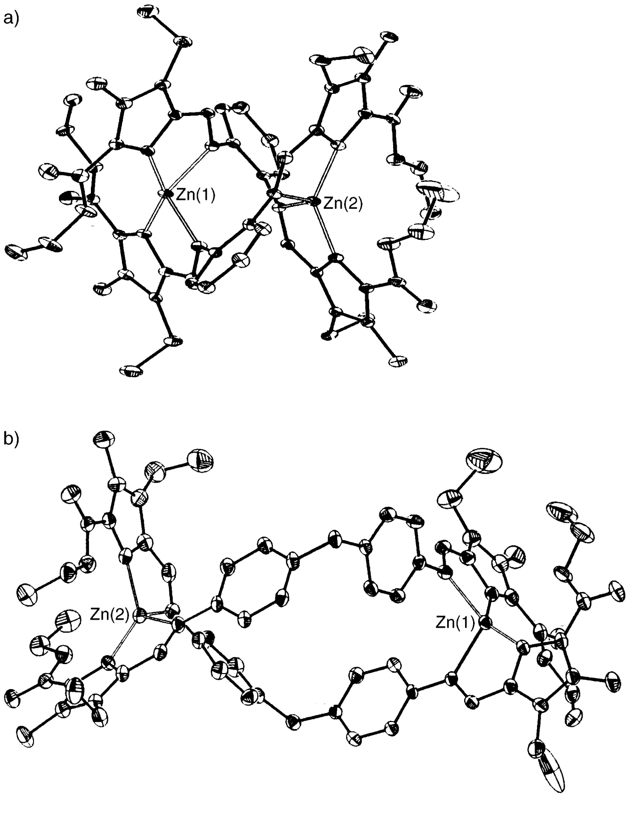

Figure 1. X-ray crystal structures of **6** (a) and **7** (b); H atoms and solvent molecules are omitted for clarity.

The X-ray structure of **8**[12] (Figure 2) displays a tetranuclear distorted square composed of four Zn^{II} ions and four ligands, with inner dimensions of 8.7×8.7 Å. All of the benzene units lie almost perpendicular to the square plane formed through the Zn centers. At each metal center, one pyrrol-2-ylmethyleneamine unit lies above the molecular plane, while the other unit lies below. The framework of compound **8** possesses D_4 geometry; two pyrrol-2-ylmethyleneamine units adopt a *trans* arrangement, which is similar to the recently reported molecular squares.[13–15] In compound **8**, the plane of the benzene ring in each ligand is slightly deviated from those of the two pyrrol-2-ylmethyleneamine units, with dihedral angles of 22.5° and 18.7°.

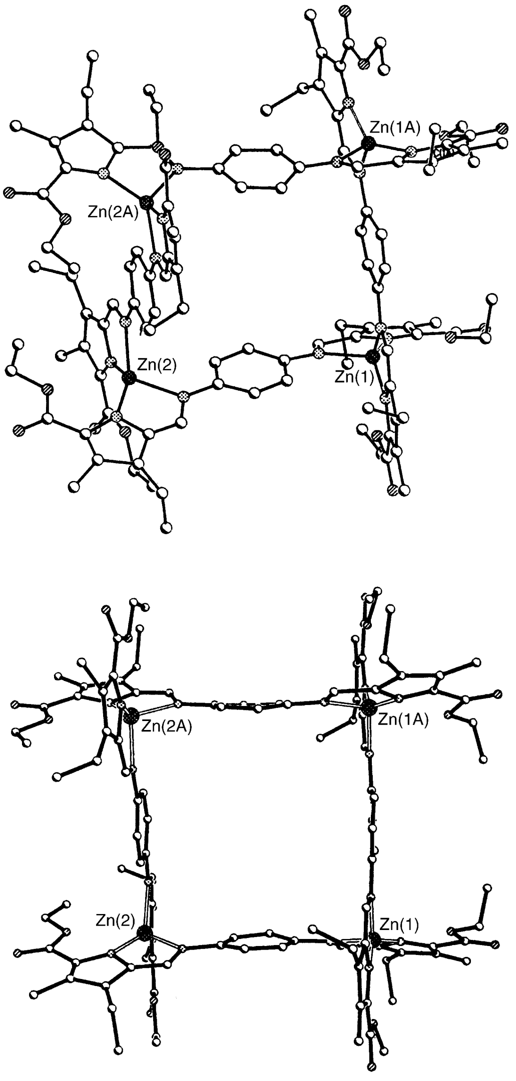

Figure 2. X-ray crystal structure of **8**; two orientations are shown, which emphasize the helical structure (above) and the cavity (below); H atoms and solvent molecules are omitted for clarity.

The X-ray analysis[16] of complex **9** (Figure 3) shows that it possesses a triangular structure. The ligands bind to the three metal centers so that one Schiff-base unit points up from the molecular plane, while the other points down. This motif is

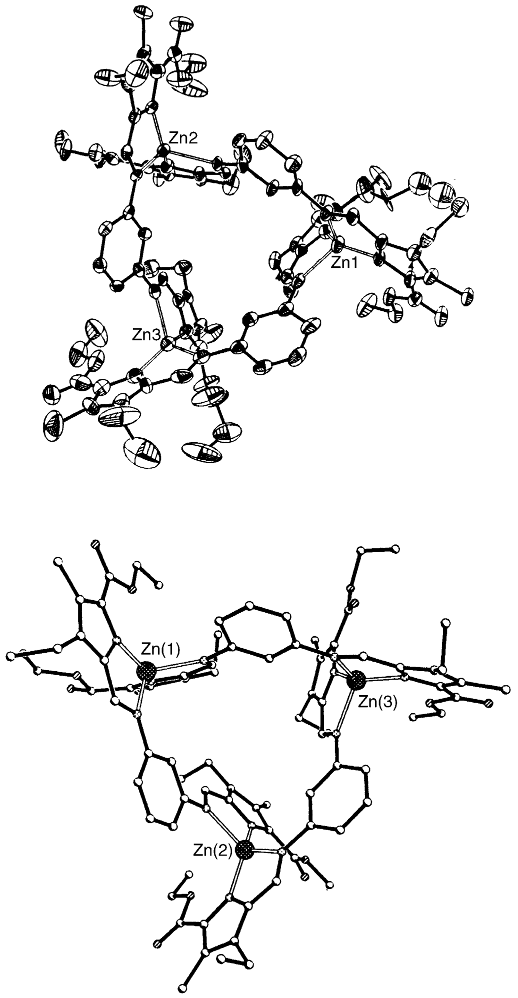

Figure 3. X-ray crystal structure of **9**; two orientations are shown, which emphasize the helical structure (above) and the cavity (below); H atoms and solvent molecules are omitted for clarity.

very similar to other recently reported triangular complexes.[17,18] The separation of the Zn atoms in the near-equilateral-triangular structure is approximately 7.5 Å. However, the overall edges of the triangle in **9** are slightly bent due to a slight deviation of the benzene ring plane from the two Schiff base planes, the dihedral angles of which are 26.3° and 2.0°.

The self-assembly of ligands **2**–**5** reflects the steric demand of the zinc ion and the arrangement of the pyrrol-2-ylmethyleneamine moieties around spacer bridges. The geometric flexibility derived from the phenyl or diphenylmethane bridges in **2**–**5** can allow the ligands to satisfy the steric requirement of the zinc ion. In all cases, a distorted coordination is mainly preferred by the zinc centers, which forces the *trans* arrangement of both halves of the bis(pyrrol-2-ylmethyleneamine) ligands.

In conclusion, we have demonstrated that pyrrol-2-ylmethyleneamine is an ideal building block for supramolecular architecture through self-assembly. It possesses similar coordinate properties to its analogues, such as dipyrrin,[18–20] and excellent solubility in common solvents. By varying the spacer bridges between two pyrrol-2-ylmethyleneamine units, the resulting bis(pyrrol-2-ylmethyleneamine) ligands can self-assemble to form supramolecules with interesting shapes, such as double-stranded helicates, triangles, and squares.

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[10] Crystal structure analyses were measured on a Rigaku R-Axis Rapid IP diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 123(2) K. Crystal data for **6**: $C_{60}H_{72}N_8O_9Zn_2$, $M_r = 1180.00$, red crystal, $0.46 \times 0.29 \times 0.23$ mm^3, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 12.4491(2)$, $b = 12.6670(3)$, $c = 20.8710(8)$ Å, $\alpha = 80.375(3)$, $\beta = 85.578(4)$, $\gamma = 61.353(3)$°, $V = 2847.65(14)$ Å^3, $\rho_{calcd} = 1.376$ g cm^{-3}, $F(000) = 1240$. A total of 17723 reflections were measured in the range $1.98 \leq \theta \leq 27.50$ (*hkl* range indices: $-15 \leq h \leq 16$, $-16 \leq k \leq 16$, $-27 \leq l \leq 27$), 11782 unique reflections (R(int) = 0.0521). The structure was refined on F^2 to $R_w = 0.1204$, $R = 0.0520$ (7232 reflections with $I > 2\sigma(I)$), and GOF = 0.907 on F^2 for 722 refined parameters.
[11] Crystal data for **7**: $C_{80}H_{99}N_8O_{11.5}Zn_2$, $M_r = 1487.41$, yellow crystal, $0.48 \times 0.28 \times 0.20$ mm^3, monoclinic, space group $P2(1)/c$, $Z = 4$, $a = 18.3613(8)$, $b = 14.7764(6)$, $c = 29.1222(13)$ Å, $\beta = 98.1140(10)$°, $V = 7822.2(5)$ Å^3, $\rho_{calcd} = 1.263$ g cm^{-3}, $F(000) = 3148$. A total of 28828 reflections were measured in the range $2.17 \leq \theta \leq 27.48$ (*hkl* range indices: $-23 \leq h \leq 23$, $-19 \leq k \leq 19$, $-37 \leq l \leq 37$), 17523 unique reflections [R(int) = 0.0553]. The structure was refined on F^2 to $R_w = 0.1500$, $R = 0.0641$ (8243 reflections with $I > 2\sigma(I)$), and GOF = 0.874 on F^2 for 899 refined parameters.
[12] Crystal data for **8**: $C_{113}H_{136}N_{16}O_{23}Zn_4$, $M_r = 2347.86$, red crystal, $0.96 \times 0.26 \times 0.22$ mm^3, tetragonal, space group $I\bar{4}2d$, $Z = 8$, $a = 30.5974(7)$, $b = 30.5974(7)$, $c = 33.0573(8)$ Å, $\alpha = \beta = \gamma = 90$°, $V = 30948.3(13)$ Å^3, $\rho_{calcd} = 1.008$ g cm^{-3}, $F(000) = 9840$. A total of 18119 reflections were measured in the range $2.48 \leq \theta \leq 27.48$ (*hkl* range indices: $-39 \leq h \leq 39$, $-28 \leq k \leq 28$, $-42 \leq l \leq 42$), 17549 unique reflections [R(int) = 0.0357]. The structure was refined on F^2 to $R_w = 0.1200$, $R = 0.0595$ (2482 reflections with $I > 2\sigma(I)$), and GOF = 0.372 on F^2 for 687 refined parameters.
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[16] Crystal data for **9**: $C_{93}H_{121}N_{12}O_{15}Zn_3$, $M_r = 1843.13$, yellow crystal, $0.79 \times 0.30 \times 0.14$ mm^3, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 15.2518(14)$, $b = 18.760(3)$, $c = 19.4142(9)$ Å, $\alpha = 74.267(4)$, $\beta = 75.913(5)$, $\gamma = 69.273(5)°$, $V = 4933.2(9)$ Å^3, $\rho_{calcd} = 1.241$ g cm^{-3}, $F(000) = 1946$. A total of 25581 reflections were measured in the range $1.61 \leq \theta \leq 27.49$ (*hkl* range indices: $-18 \leq h \leq 19$, $-24 \leq k \leq 24$, $-25 \leq l \leq 25$), 18924 unique reflections [R(int) = 0.1206]. The structure was refined on F^2 to $R_w = 0.1530$, $R = 0.0738$ (4351 reflections with $I > 2\sigma(I)$), and GOF = 0.701 on F^2 for 1062 refined parameters.

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[21] CCDC-199238 (**6**), -199237 (**7**), -199239 (**8**), and -200320 (**9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).