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The Use of Dipyrromethene Ligands in Supramolecular Chemistry

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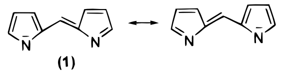
The preparation of supramolecular architectures is currently a subject of considerable interest as an approach to materials with novel physicochemical properties.[1] One aspect of this field is the self-assembly of coordination complexes from suitable ligands and metal ions.[2] To this end, a variety of three-dimensional inorganic arrays such as helicates,[3] grids,[4] cages,[5] ladders,[6] and rings[7] have been prepared from polybipyridine ligands and transition metal ions. Additionally, several multiporphyrin structures have been reported, including those resulting from self-assembly with metal−ligand binding[8] and hydrogen bonding.[9] As part of our ongoing research in the fields of porphyrin and pyrrole chemistry, we are investigating the use of dipyrromethenes as ligands in supramolecular coordination chemistry. We herein report novel helicate and trimeric structures, obtained by the self-assembly of appropriately designed ligands and transition metals.

Several supramolecular architectures formed by multicomponent self-assembly with polybipyridine ligands have been reported.[3−7] Due to the nature of the ligands (neutral), these complexes are charged species. Therefore, to isolate and characterize the architectures, counterions must be used to generate neutral compounds. This may result in competitive binding between the counterion and the ligand, which is usually overcome by the use of specific noncoordinating counterions. Unfortunately, this type of counterion often gives rise to considerable disorder in the solid state. Our efforts in this field are aimed toward the preparation of uncharged supramolecular architectures, in which counterions are not required.


(1)

Dipyrromethenes **(1)** are fully conjugated flat bipyrrolic moieties. As such, they are useful ligands for chelation to transition metals.[10] Consequently, polydipyrromethenes, in which multiple dipyrromethenes are linked directly or by a bridge, such as methylene, ethylene, etc., are potential ligands for coordination with transition metal ions to form well-defined architectures through self-assembly. A mixture of zinc:octaethyl formylbiliverdinate complexes 1:1 and 2:2 was reported by Fuhrhop[11] et al. and the crystals were separated by hand. X-ray crystallography showed that the 2:2 complex exists as a helix. Similarly, the helical X-ray structure of the zinc complex of 1,2,3,7,8,12,13,17,18,19-decamethyl-biladiene-a,c has been reported.[12] In 1965 one of us[13] suggested that a 2:2 (ligand **2**:Co^{II}) complex existed in a helical conformation[14] and a year later that the 2:2 (ligand **3**:Cu^{II}) complex had a similar structure.[15]

To reinvestigate and explore the use of dipyrromethenes in self-assembly processes and investigate the impact of spacer between dipyrromethene units, we reacted the hydrobromide salts **4**, **5**, and **6** with $Zn(OAc)_2$ or $Co(OAc)_2$ in $CHCl_3$/MeOH (Scheme 1).[16] Dimers **7**, **8**, and **9** were obtained after chromatography. EI mass spectroscopy gave the molecular masses for these complexes to be 1035, 1162, and 1078, respectively, which corresponds, in each case, to a metal:ligand ratio of 2:2.

The X-ray structure (Figure 1) of cobalt complex **8** shows that this compound has double-stranded helical geometry, resulting from a major twist around the linking methylene bridge in the biladiene strands.[17] This twist effectively divides the ligand into two dipyrromethene subunits, each bonded to a different Co^{II} ion. As a result, each Co^{II} center and its two dipyrromethene segments (originating from different ligands) have an almost tetrahedral geometry, which is very similar to that of the cobalt complex of simple dipyrromethenes,[10,18,19] although the bond angles and bond lengths indicate a small deviation from tetrahedral geometry.[16] Similarly, the X-ray structure (Figure 2) shows **7** to crystallize as a helix, satisfying the tetrahedral coordination geometry of each Zn^{II} center.[20] The parameters of these two structures are very similar. However, as a result of differing spacer length, two main differences occur. The angle between the flat dipyrromethenes in the same strand changes from 89° in complex **8** to 108° in complex **7**. Correspondingly, the distance between two metal centers within each helix is different, being 4.33 Å in **8** and 4.89 Å in **7**. This indicates that the spacers play a key role upon the exact parameters of these helical structures. Further investigation is directed toward the identification of the structure of the complexes resulting from ethylene-linked ($n = 2$) polydipyrromethenes.

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(16) See Supporting Information for further details.

(17) Crystal data for **8**: green plate, triclinic, space group P (No. 2), $a = 12.306(2)$ Å, $b = 14.666(3)$ Å, $c = 19.939(6)$ Å, $\alpha = 86.751(7)°$, $\beta = 76.853(4)°$, $\gamma = 66.157(2)°$, $V = 3202.6(11)$ Å^3, $Z = 2$, $T = -93$ °C, Rigaku/ADSC CCD diffractometer, Mo Kα radiation ($\lambda = 0.71069$ Å), $2\theta_{max} = 50.7°$, R (on F, 3151 reflections with $I = 3\sigma(I)$) = 0.070, R_w (on F^2, all 10991 unique reflections) = 0.150, gof(F^2) = 1.56, 721 variables.

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(20) Crystal data for **7**: metallic green irregular crystal, orthorhombic, space group *Fddd* (No. 70), $a = 14.3337(12)$ Å, $b = 26.1271(4)$ Å, $c = 28.7758(7)$ Å, $V = 10776.5(7)$ Å^3, $Z = 8$, $T = -93$ °C, Rigaku/ADSC CCD diffractometer, Mo Kα radiation ($\lambda = 0.71069$ Å), $2\theta_{max} = 61.0°$, R (on F, 2290 reflections with $I = 3\sigma(I)$) = 0.039, R_w (on F^2, all 3955 unique reflections) = 0.071, gof(F^2) = 1.58, 159 variables.

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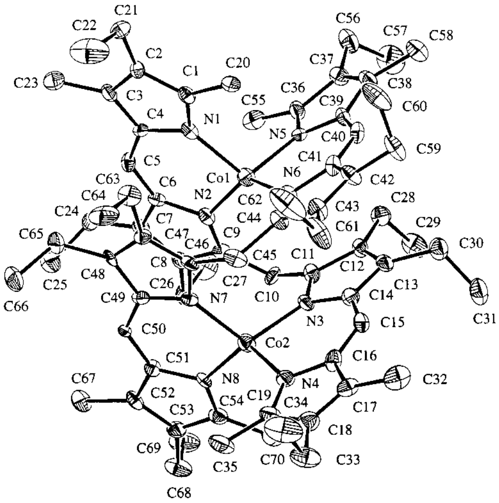


Figure 1. X-ray structure of **8** (H atoms omitted for clarity).

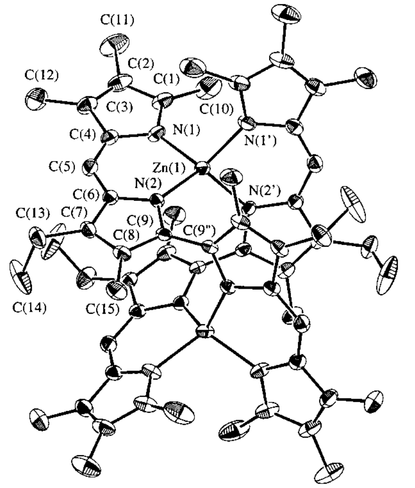
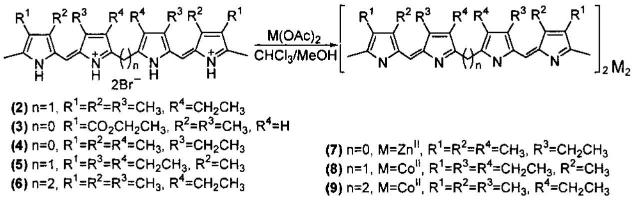
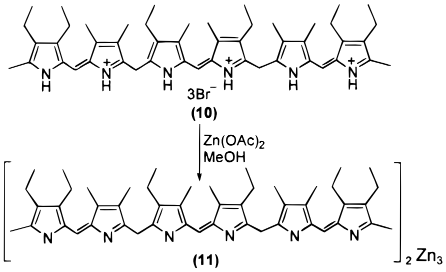


Figure 2. X-ray structure of **7** (H atoms omitted for clarity).

Scheme 1



Scheme 2



Molecular modeling[21] showed all the simulated complex structures to have helical double-stranded geometry. The structures obtained by simulation of complexes **8** and **7**, respectively, are extremely similar to the X-ray structures as shown by comparison of the structural parameters in Table 1. The strong correlation between the actual (X-ray) and simulated parameters indicates the usefulness of this type of modeling for these complexes.

Table 1. Selected Structural Parameters of X-ray and Simulated Structures of Complexes **7** and **8**

	complex **7**			complex **8**	
	X-ray	model		X-ray	model
bond angle (deg)					
N1−Zn−N2	95.53	102.01	N1−Co1−N2	98.7	103.4
N1−Zn−N1′	106.32	108.75	N1−Co1−N5	108.3	110.3
distance (Å)					
Zn−Zn	4.890	4.766	Co−Co	4.331	4.465
torsion angle (deg)					
N2−C9−C9′−N2′	−112.3	−110.6			

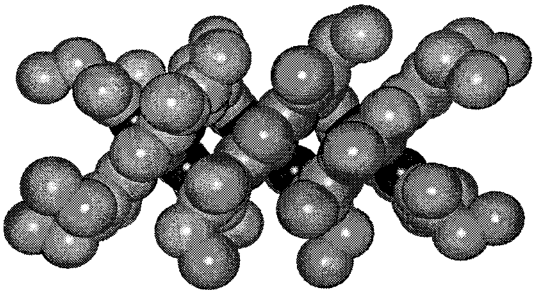


Figure 3. Space filling representation of **11** obtained with HyperChem (Release 5.01 for Windows).[21] For clarity, all H atoms have been omitted.

Having successfully prepared several binuclear complexes, we further extended our work to larger architectures, namely trinuclear arrays of metals, held together by helically arranged methylene-bridged dipyrromethenes. Zn^{II} complex **11** was prepared by refluxing **10** and $Zn(OAc)_2$ in methanol, followed by chromatography. EI mass spectroscopy showed the product to have a molecular mass of 1663, which corresponds to the trinuclear bisligand complex, with a Zn:ligand ratio of 3:2. Structural simulation as before indicates that it also exists as a helical double-stranded structure as shown in Figure 3.

Having shown that helical structures may be obtained by complexation of ligands comprised of two dipyrromethene units linked at the α-position, we extended this work to include those directly linked at the *β*-position. To our surprise, these ligands gave trimeric metal complexes with a ligand:metal ratio of 3:3. Future work aims to identify the structure of these trimers and assess the crucial factors affecting helical vs trimer construction.

In summary this communication reports the synthesis of novel helical and trimeric complexes, serving as an entry point for the use of dipyrromethenes in self-assembly and supramolecular chemistry. The metal complexes are uncharged, thus making their isolation facile, via chromatography if necessary, without the need for counterions. Actual geometric data obtained from a crystal structure have been compared to data obtained from molecular modeling, and the results are extremely similar, thus validating this type of modeling for these compounds. Current work is aiming to further our understanding of self-assembly processes with dipyrromethene ligands, for the construction of novel grids, ladders, and supramolecular helicates.

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Supporting Information Available: Experimental and spectroscopic data for **7**−**11** and full details of the structure analyses, atomic coordinates and equivalent isotropic thermal parameters, hydrogen atom parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, intermolecular contacts, and least-squares planes for **7** and **8** (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[21] HyperChem Release 5.01 MM+ force field optimized by Polak-Ribiere.