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# Self-assembly of novel trimers using dipyrromethene ligands

Alison Thompson, Steven J. Rettig† and David Dolphin\*

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada V6T 1Z1

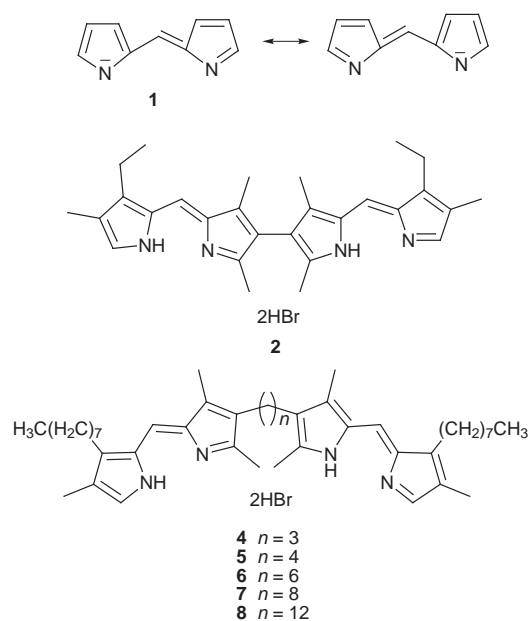
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Ligands comprising two dipyrromethene units linked at the  $\beta$ -position have been used to prepare trimeric complexes with  $Zn^{II}$  and  $Co^{II}$ ; the structure of the  $Zn^{II}$  complex is confirmed by X-ray analysis.

The self-assembly of supramolecular structures by complexation chemistry utilizing metal ions and suitable ligands is one approach to new structures with unusual and interesting properties.<sup>1</sup> Three-dimensional inorganic arrays have been forthcoming, giving helicates,<sup>2</sup> grids,<sup>3</sup> cages,<sup>4</sup> ladders<sup>5</sup> and rings,<sup>6</sup> through the coordination chemistry of polybipyridine ligands and transition metal ions. Multi-porphyrin structures have also been reported.<sup>7</sup> Dipyrromethenes, the building blocks of porphyrins, are themselves interesting ligands for supramolecular coordination chemistry and we have been able to rationally design new architectures through self-assembly of these ligands and transition metal ions.

Metal complexes generated from polybipyridine ligands<sup>2–7</sup> are rendered neutral by the use of counter-ions. This may give rise to problematic isolation procedures, or induce disorder in the solid state. Our efforts in this field are aimed towards the preparation of uncharged supramolecular architectures, in which counter-ions are not required. The dipyrromethene unit **1** is a useful ligand in metal chelation,<sup>8</sup> as it is a monoanionic ligand and the pyrrolic moieties are coplanar. Indeed, preliminary investigations in our group have shown that dipyrromethene units linked at the  $\alpha$ -position can be used to generate helical complexes.<sup>9</sup> We sought to design ligands comprising linked dipyrromethene binding units, with which to construct neutral three-dimensional structures, including grids and ladders.

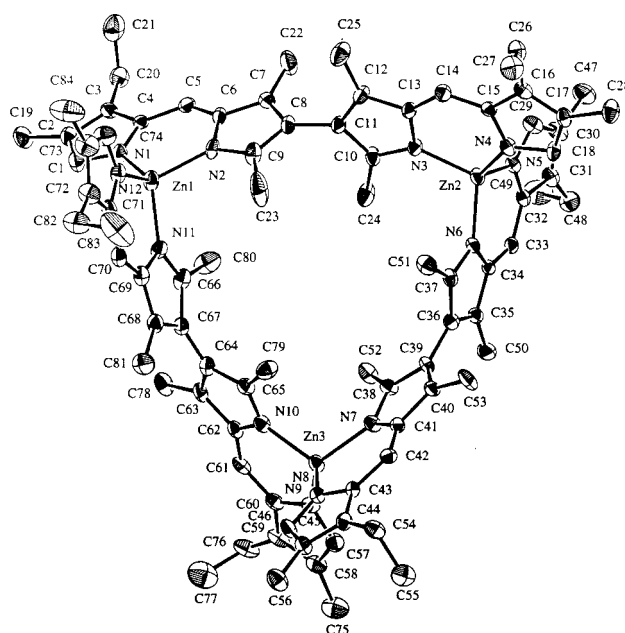
When a solution of  $Zn(OAc)_2$  and NaOAc in MeOH was added to a solution of **2**<sup>10</sup> in  $CHCl_3$  a single complex **3** was



formed in high yield. § EI mass spectroscopy showed the molecular mass of the product to be 1468, which corresponds to the trimeric complex with a ligand : metal ratio of 3 : 3. The X-ray structure¶ of the trinuclear complex (Fig. 1) shows that it crystallizes in a triangular fashion, with the ligands linking the three metal centers overlapping, in a progressive manner: in each ligand, one dipyrromethene binding unit lies above the averaged plane of the molecule, whilst the other dipyrromethene unit lies below the averaged plane. The distances between the three metal centers are 9.27, 9.34 and 9.36 Å. Each metal center has distorted tetrahedral geometry in order to permit the triangular arrangement. Selected N–Zn–N angles are shown in Fig. 1. The six planar dipyrromethene sub-units lie at 63.6, 85.6 and 68.7° to their partner dipyrromethene unit within the same ligand.

Similarly, **2** was reacted with  $Co(OAc)_2$  to give the corresponding cobalt trimer, with molecular mass of 1449, again in high yield. Several reaction conditions were applied to these preparations including temperature variations (–10 °C to reflux in MeOH) and different lengths of addition period (metal salts added in one portion, to over 24 h). In each and every case, the same trimers were formed in high yield, suggesting them to be both the kinetic and thermodynamic products.

Continuing with the theme of pyrroles linked at the  $\beta$ -position, we subjected several hydrobromide salts **4–8** with varying hydrocarbon spacer lengths ( $n = 3, 4, 6, 8, 12$ ) between the  $\beta$ -positions<sup>10</sup> to standard complexation reactions with  $Zn(OAc)_2$ . Complexation was almost quantitative for each ligand. Table 1 shows that as the length of the hydrocarbon chain between the pyrrole moiety increases, so formation of the



**Fig. 1** X-Ray structure of **3** (hydrogen atoms and 2  $CHCl_3$  molecules of crystallization are omitted for clarity). Selected bond angles (°): N(1)–Zn(1)–N(2) 95.5(2), N(1)–Zn(1)–N(12) 116.4(2), N(1)–Zn(1)–N(11) 119.7(2), N(2)–Zn(1)–N(11) 111.3(2), N(2)–Zn(1)–N(12) 119.7(2), N(11)–Zn(1)–N(12) 96.0(2).

† Deceased October 27, 1998.

**Table 1** Oligomeric ratios of metal complexes

Salt	<i>n</i>	Monomer : dimer : trimer <sup>a</sup>
<b>2</b>	0	0 : 0 : 1
<b>4</b>	3	0 : 1 : trace
<b>5</b>	4	0 : 1 : trace
<b>6</b>	6	1 : 1 : trace
<b>7</b>	8	1 : trace : trace
<b>8</b>	12	1 : 0 : 0

<sup>a</sup> Traces of higher oligomers were also observed for ligands **4**, **5** and **6**.

monomer dominates, as determined by MALDI spectroscopy. Molecular modeling<sup>11</sup> rationalizes this, as the longer spacer length allows the dipyrromethene units to fold back against each other, thus fulfilling the tetrahedral geometry requirements for binding to the metal ion. In the case of the ligand derived from salt **2** (*n* = 0) this folding is clearly not allowed and the trimer is formed. For **4** and **5** (*n* = 3 and 4, respectively) the spacer chain length permits sufficient folding for the corresponding dimers to be formed, but when *n* = 6 or greater, folding is sufficient to allow the monomer to form. However, MALDI spectroscopy showed small amounts of higher order complexes (trimers–hexamers) to be present in each case. Variation of reaction conditions did not alter the oligomeric ratio of products.

In summary, we have demonstrated the usefulness of linked dipyrromethene ligands in the self-assembled preparation of uncharged novel architectures. The properties of the trimeric complexes will be reported at a later date. Current work is focussed towards the construction of novel grids, ladders and supramolecular helicates using dipyrromethene ligands.

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## Notes and references

‡ Selected data for **2**: mp >230 °C (decomp.);  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  506;  $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3)$  1.23 (3H, t, *J* 7, CH<sub>3</sub>), 2.13 (3H, s, CH<sub>3</sub>), 2.20 (3H, s, CH<sub>3</sub>), 2.58 (3H, s, CH<sub>3</sub>), 2.72 (2H, q, *J* 7, CH<sub>2</sub>), 7.72 (1H, s, CH), 13.40 (1H, br s, NH), 13.60 (1H, br s, NH);  $\delta_{\text{H}}[200 \text{ MHz}; (\text{CD}_3)_2\text{CO}]$  1.24 (3H, t, *J* 7, CH<sub>3</sub>), 2.18 (3H, s, CH<sub>3</sub>), 2.37 (3H, s, CH<sub>3</sub>), 2.89 (2H, q, *J* 7, CH<sub>2</sub>CH<sub>3</sub>), 7.67 (1H, s, CH), 7.78 (1H, s, CH), 8.12 (1H, br s, NH);  $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3)$  9.79 (CH<sub>3</sub>), 11.02 (CH<sub>3</sub>), 13.49 (CH<sub>3</sub>), 16.03 (CH<sub>3</sub>), 18.32 (CH<sub>2</sub>), 121.06, 121.82 (CH), 125.02, 126.92, 127.29, 142.47 (CH), 145.03, 149.41, 155.63; *m/z* EI 426 [(M<sup>+</sup> – 2HBr) 55%], 411 (74, M – 2HBr – Me), 397 (48, M – 2HBr – Et), 213 [3, (M – 2HBr)<sup>2+</sup>], 94 (100) (Found: M<sup>+</sup> – 2HBr, 426.2778. C<sub>28</sub>H<sub>34</sub>N<sub>4</sub> requires 426.2784).

§ Experimental: a solution of Zn(OAc)<sub>2</sub> (105 mg, 0.476 mmol) and Na(OAc)<sub>2</sub> (65 mg, 0.476 mmol) in MeOH (2 cm<sup>3</sup>) was added to a solution of ligand **2** (56 mg, 0.095 mmol) in CHCl<sub>3</sub> (2 cm<sup>3</sup>) and the reaction mixture stirred at room temperature for 4 h. The solvents were removed *in vacuo* and the resulting solid dissolved in CHCl<sub>3</sub> (10 cm<sup>3</sup>) and filtered through a short plug of Celite. The solution was then washed with water (3 × 10 cm<sup>3</sup>), dried over MgSO<sub>4</sub> and the solvent removed *in vacuo* to give **3** (40 mg, 86%) as a green metallic solid, *R*<sub>f</sub> (3:1 hexane:CH<sub>2</sub>Cl<sub>2</sub>) 0.4; mp >230 °C (decomp.);  $\lambda_{\max}(\text{CH}_2\text{Cl}_2)/\text{nm}$  522;  $\delta_{\text{C}}(75 \text{ MHz}; \text{CDCl}_3)$  10.21 (CH<sub>3</sub>), 11.12 (CH<sub>3</sub>), 14.44 (CH<sub>3</sub>), 16.65 (CH<sub>3</sub>), 18.22 (CH<sub>2</sub>), 122.78 (CH), 123.33,

123.93, 136.23, 136.95, 140.32, 142.58, 147.22 (CH), 159.10; *m/z* EI 1468 (M<sup>+</sup>, 100%), 734 (50, M<sup>2+</sup>), 490 (3, M<sup>3+</sup>) (Found: M<sup>+</sup>, 1468.5752. C<sub>84</sub>H<sub>96</sub>N<sub>12</sub>Zn<sub>2</sub> requires 1468.5791).

¶ Crystal data for **3**: C<sub>84</sub>H<sub>96</sub>N<sub>12</sub>Zn<sub>2</sub>·2CHCl<sub>3</sub>, *M* = 1708.66, triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 14.251(3), *b* = 18.7667(9), *c* = 19.684(2) Å,  $\alpha$  = 63.2582(11),  $\beta$  = 80.2531(15),  $\gamma$  = 68.169(2)°, *U* = 4364.1(8) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.300 g cm<sup>-3</sup>. Rigaku AFC7/ADSC Quantum 1 CCD diffractometer, *T* = 180 K, graphite-monochromated Mo-K $\alpha$  radiation,  $\lambda$  = 0.71069 Å,  $2\theta_{\max}$  = 50.4°, 35289 reflections measured, 15359 unique (*R*<sub>int</sub> = 0.051). The final unit-cell parameters were obtained by least-squares using 20163 reflections with  $2\theta$  = 4.0–50.4°. Data were corrected for Lorentz polarisation and absorption (multi-scan including decay and scaling, relative correction factors 0.89–1.00). The structure was solved by the Patterson method. One CHCl<sub>3</sub> molecule was modeled as (3:1) two-fold disordered; the carbon atom associated with the minor component could not be located and was not included in the model. Non-hydrogen atoms [except Cl(9)] were refined with anisotropic thermal parameters and hydrogen atoms were fixed in calculated positions with C–H = 0.98 Å. The refinement converged at *R* [*F*, 7705 reflections having *I* ≥ 3σ(*I*)] = 0.062 and *R*<sub>w</sub> (*F*<sup>2</sup>, all 15359 unique reflections) = 0.129. Calculations were performed using the *teXsan* structure analysis package (Molecular Structure Corporation, 1985–1997). CCDC 182/1158.

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