A triple-stranded helicate and mesocate from the same metal and ligand†

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A pair of triple-stranded helicates and mesocates were, for the first time, isolated from the same reaction of a novel α-free bis(dipyrromethene) ligand with either Co$^{3+}$ or Fe$^{3+}$.

Dinuclear triple-stranded M$_2$L$_3$ complexes, which are some of the simplest octahedral multinuclear assemblies, can serve as models for understanding supramolecular chemistry relating to aspects of self-recognition and chirality control. Over the past two decades, this field has been studied using various ligands such as bis(bipyridine), dicatechol and benzimidazole derivatives. However, triple-stranded bis(dipyrromethene) complexes which would serve to generate attractive uncharged systems have so far gone unreported, even though mononuclear octahedral dipyrmethene complexes have been described. In previous work, several interesting well-defined architectures with tetrahedral geometry such as double and triangular helicates have been synthesized from a series of α-substituted poly(dipyrromethene) ligands. Interest in novel uncharged poly(dipyrromethene) supramolecular systems built upon octahedral geometries prompted us to investigate the synthesis of triple-stranded M$_2$L$_3$ complexes.

Depending upon the chirality at each metal centre, dinuclear triple-stranded octahedral M$_2$L$_3$ complexes may exhibit three configurations: ΔΔ, ΔΛ and ΔΔ, which result in two possible architectures: homochiral helicates (ΔΔ and ΔΛ) and achiral mesocates (ΔΔ). Helicates, generated as racemic mixtures when non-chiral ligands are used, are favoured products in most cases, while the diastereomeric mesocates are less common. It was not until 1995, almost two decades after a doublet at 3.25 and 3.36 ppm. Given the methylene hydrogens were assigned with certainty, peak multiplicity is not observed and the peaks cannot be differentiated from one another. The mean N–Co bond length is 1.937 Å for the mesocate and 1.948 Å for the helicate.

Since all but one of the known mononuclear octahedral dipyrmethene complexes were synthesized using α-free substrates, a novel α-free bis(dipyrromethene) ligand (LH$_2$2HBr) was designed for the purpose of obtaining dinuclear triple-stranded complexes. However, due to the poor stability of 3, we were required to work at low temperature in order to obtain the proligand from the condensation of the β,β′-linked diformyl-dipyrromethene 1$^9$ and 3,4-diethyl pyrrole 2 (Scheme 1). The rapid metallation of a fresh solution of 3 with Co$^{3+}$ (or Fe$^{3+}$) produced a dark red solution from which the non-polar complexes were collected by flash chromatography on a short column with a yield of 42% (Co$^{3+}$) and 22% (Fe$^{3+}$), respectively. The low yields result from the instability of the ligand at the temperatures required for metallation; subsequent chromatography on a one-metre long silica gel column ultimately afforded two products (A-type and B-type) in a rough ratio of 3 : 2, for both metals.

The two types of complexes displayed very similar properties such as solubility and polarity. Nevertheless, the B-type complexes are slightly more polar, which enabled their separation from A-type complexes.

MALDI-TOF mass spectroscopy indicated that both A-type and B-type complexes had the same mass corresponding to M$_2$L$_3$. In the case of the diamagnetic Co$^{3+}$ complexes, the $^1$H NMR spectrum of 4 shows a singlet for the spacer CH$_2$ hydrogens at 3.51 ppm while those of 5 exhibit two sets of doublets at 3.25 and 3.36 ppm. Given the methylene hydrogens of the spacer would be homotopic in a D$_3$ helicate, but diastereotopic in a C$_{2v}$ mesocate, A-type and B-type complexes are helicates and mesocates, respectively. The $^1$H NMR of the paramagnetic Fe$^{3+}$ complexes were also detected but over a much wider range (−30 to +30 ppm). Although the peak multiplicity is not observed and the peaks cannot be assigned with certainty, 7 exhibits two small peaks at 9.53 and 5.36 ppm, indicating it is a mesocate and 6 is a helicate.

The structures of the helicates and mesocates were further confirmed by X-ray diffraction analysis (Fig. 1). For all four complexes, each trivalent metal is octahedrally coordinated to three dipyrmethene segments which are roughly perpendicular to each other. The mean N–Co bond length is 1.937 Å for 4 and 1.948 Å for 5, very close to the mean N–Co (1.945 Å) of a previously reported mononuclear octahedral dipyrmethene complexes. Considering the mean bond lengths, however, 4 − 6 are helicates while 7 is a mesocate.

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‡ These results are consistent with those reported by Kotila.4 Four years later, Raymond's group reported the isolation of both a triple-stranded helicate and mesocate in thermodynamic equilibrium in solution.7 To the best of our knowledge, the isolation of both diastereomers generated from the same metal and ligand has not hitherto been reported. Recently, we have captured both triple-stranded helicates and mesocates in the reactions of a novel α-free bis(dipyrromethene) ligand with either Co$^{3+}$ or Fe$^{3+}$.
The mean N–Fe bond length of \( \mathbf{6} \) is 1.968 Å and that of \( \mathbf{7} \) is 1.970 Å; both are slightly longer than that reported for a monomeric complex (1.967 Å). For the helicates, the twist angle, the rotation angle between the two metal centres, is 101° for \( \mathbf{4} \) and 98° for \( \mathbf{6} \), causing a 27.9 and 29.3 Å helical pitch, respectively. Due to the different wrapping of the strands, the spacer C–C–C bond angles of helicates were 1.8° and 2.8° greater than those of the mesocates \( \text{Co}_2\text{L}_3 \) and \( \text{Fe}_2\text{L}_3 \), respectively. However, the distances between the two metal centres of the helicates were interestingly shorter than those of the mesocates in both cases.

Because of their structural similarity, the optical spectra of the helicates and mesocates are very similar. As shown in Fig. 2, the absorption spectra of \( \mathbf{4} \) and \( \mathbf{5} \) or \( \mathbf{6} \) and \( \mathbf{7} \) are similar in shape except the helicates \( \mathbf{4} \) and \( \mathbf{6} \) are slightly bathochromically-shifted and have a small shoulder between 550 and 570 nm.

A striking finding of this work is that the triple-stranded bis(dipyrromethene) helicates and mesocates do not interconvert even upon heating to 150 °C in solution. In contrast, Raymond’s group found that both mononuclear \(^{13}\) and dinuclear \(^{3c}\) catechol complexes readily isomerized in solution through a non-dissociative intramolecular Bailar twist. \(^{14}\) The same group also observed a pair of bis-hydroxypyridinone helicate and mesocate complexes in thermodynamic equilibrium in solution. \(^{7}\) As shown in Fig. 3, the hydroxypyridinone coordinating unit, having an open unhindered structure, can readily achieve a \( D_{3h} \) intermediate required of a Bailar twist (b in Fig. 3) without breaking any ligand–M bond. However, in the case of the bis(dipyrromethene) complexes reported here, both non-dissociative intermediates resulting from either a Bailar twist or Ray–Dutt twist \(^{14}\) represent considerable steric overlap between the \( \alpha \)-hydrogens and are thus unfavoured (Fig. 4). Moreover, an alternative interconversion pathway through ligand dissociation is also not favoured, since breaking at least two strong Met–N bonds would be required and Thompson’s group\(^{15}\) has shown, using chiral \( M_2\text{L}_2 \) complexes, that such dissociative processes do not readily occur.

The formation of helicate \( \text{versus} \) mesocate has been a topic of interest since the debut of mesocates. \(^{3b,3f,7,16,17}\) Although the odd–even rule \(^{16}\) is valuable in many cases, our work shows that even ligands with a single methylene spacer can form both mesocate and helicate with the same metal. Therefore, the length of a spacer cannot be relied on for predicting the formation of helicate \( \text{versus} \) mesocate.

In summary, we have established the first synthesis of dinuclear octahedral poly(dipyrromethene) complexes where both triple-stranded helicates and mesocates were generated and isolated from the same reaction.
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Notes and references


10 $R_t = 0.730$ for 4; 0.694 for 5; 0.730 for 6; 0.694 for 7 if 1:1 (v:v) methylene chloride–hexanes was used as the developing solvent.

11 The mean spacer C–C–C bond angles are 114.4 $\pm$ 0.730 for 4; 115.2 $\pm$ 0.694 for 5; 112.4 $\pm$ 0.730 for 6; 112.4 $\pm$ 0.694 for 7.

12 Metal-metal distances are 7.817 Å in 4; 8.138 Å in 5; 7.965 Å in 6; 8.140 Å in 7.


