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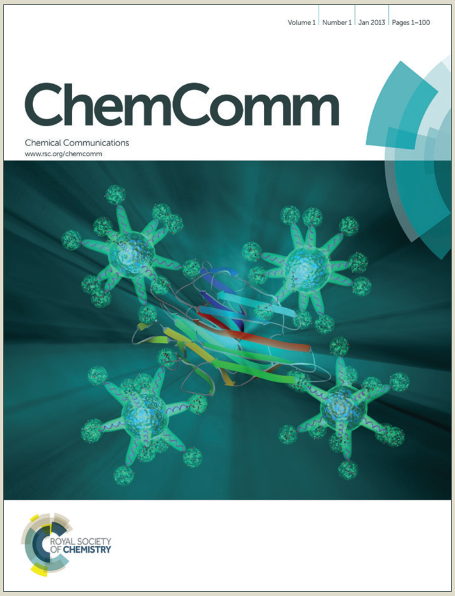

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On Zn(II) 2,2'-bisdipyrrin circular helicates

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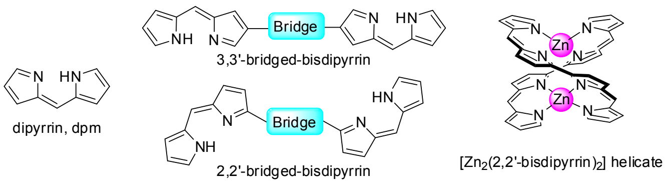
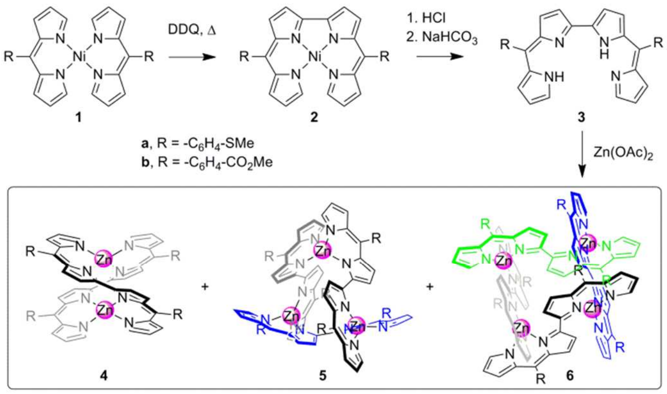
Coordination of two 2,2'-bisdipyrrin ligands, bearing methyl ester or methylthioether peripheral groups, with Zn(II) cations leads not only to the formation of the expected linear helicates but also concomitantly to novel tri- and tetra-nuclear circular species that have been isolated and fully characterized in solution and by X-Ray diffraction.

Over the past decades, molecular polygons, cages, knots and helicates have been intensively studied, owing to their potential application in catalysis, magnetism and optics.[1,2] In particular, helicates have been widely investigated and numerous examples of linear helices have been reported.[2] However, circular analogues, in which the metal cations define a polygon with the ligands wrapping over and under, are rather rare and their formation remains challenging.[3] The vast majority of ligands employed for the preparation of such species comprises the pyridine moiety.[3] In contrast, the use of the bis-pyrrolic unit, dipyrrin (dpm, Scheme 1),[4] for the preparation of cyclic helicates has been almost unexplored. This is surprising given that dpm derivatives have demonstrated their ability to form homo- and hetero-metallic coordination polymers[5] as well as discrete architectures,[6-10] such as molecular polygons and polynuclear grids.[7] Ligands based on 2,2'- and 3,3'-bisdipyrrin form linear binuclear helicates especially with Zn(II) cation (Scheme 1).[8-10] Dolphin *et al.* have reported that the formation of a trinuclear complex using a bis-dpm ligand for which the two dipyrrin moieties are directly connected at positions 3 and 3'.[7a] However, this kind of architectures has, to our knowledge, not been reported for 2,2'-bis-dpm derivatives, although this type of connectivity between the two dpm moieties (angular restriction) should also lead to the formation of higher nuclearity cyclic complexes and in particular circular helicates.



Scheme 1 Representation of a dipyrrin, 2,2'- and 3,3'-bis-dipyrrin derivatives and a Zn(II) linear double helicate based on a 2,2'-bisdipyrrin ligand

We report here that, indeed, under certain reaction conditions, 2,2'-bis-dpm based binuclear linear helicates are formed concomitantly with tri- and tetranuclear circular complexes. These species, obtained using two novel ligands, were fully characterized in solution by ^{1}H and DOSY NMR and UV-Visible spectroscopies, mass spectrometry and by single-crystal X-Ray diffraction in the solid state.



Scheme 2 Synthetic route for the formation of linear helicate **4**, tri- and tetra-nuclear circular helicates **5** and **6**.

Aiming at the development of new 2,2'-bis-dpm derivatives for the preparation of heterometallic architectures, we have been interested in the preparation of ligands **3a** and **3b** (Scheme 2) bearing either methylthioether or methyl ester groups respectively. The synthetic pathway followed the Ni-templated strategy reported by Scott and coworkers (Scheme 2, for details see ESI).[11] Complexes **1a** and **1b**, prepared as described,[12] were reacted with DDQ in refluxing toluene to afford **2a** and **2b** in 69% and 36% yields respectively. Demetallation of the latter by treatment with HCl, followed by Na_2CO_3, gave 2,2'-bis-dpms **3a** and **3b** both in 89% yield. Upon reacting overnight these ligands with one equivalent of $Zn(OAc)_2(H_2O)_2$ in either pure $CHCl_3$ or a $CHCl_3$/MeOH (4/1) mixture, the expected binuclear helicates **4a** and **4b** were obtained in 92% and 98% yield respectively. Interestingly, when the reaction was performed in $CHCl_3$/MeOH (1/4), the formation of a precipitate was observed, from which another complex, **5**, could also be isolated. Further optimization of the synthetic conditions (reaction time, solvent nature and ratio) showed that in addition to compounds **4** and **5**, a third, minor, compound **6**, is formed upon

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performing the complexation in CH_2Cl_2/MeOH (1/4) over 30 minutes with either ligands. Work-up and column chromatography allowed the isolation of these complexes in pure form (see ESI). However, it should be noted that, with the methylthioether ligand **3a**, the minor compound **6a** was only present as traces. ^{1}H-NMR spectroscopy indicated that **5a**, **5b** and **6b** are symmetrical species. Investigations by mass spectrometry revealed that they are tri- $[Zn_3(2,2'\text{-bis-dpm})_3]$ and tetra-nuclear $[Zn_4(2,2'\text{-bis-dpm})_4]$ complexes respectively (ESI). The trinuclear compound **5a** was obtained in 24% yield, whereas **5b** and **6b** were isolated in 15 and 9% yield respectively. Compounds **1a**-**5a** and **1b**-**6b** have been characterized by standard analytical techniques as well as by single-crystal X-Ray diffraction (ESI). Unfortunately, compound **6a**, assigned by analogy with **6b** to a tetranuclear species, was only detected as a trace on TLC plate and could not be further characterized. Comparison of the structures of the Ni complexes of the types **1** and **2** highlights the effect of the bond formation between the two dpm chelates (Fig. 1). The Ni(II) cation undergoes a change in its coordination geometry from pseudo-tetrahedral to distorted square planar. For example, this is illustrated by the angle between the two bipyrrolic moieties decreasing from 56.2° in **1b** to 23.6° in **2b**. Whereas the Ni-N bond distances in **1b** are in a narrow 1.8791(16) - 1.8947(16) Å range, in agreement with a reported polymorphic structure of this compound,[12a] these distances are different (1.8496(14) *vs* 1.8940(13) Å) for **2b**, as observed for other Ni(2,2′-bisdipyrrin) complexes.[8h,11,13] In the structure of ligand **3b**, the two dipyrrin chelates feature intramolecular hydrogen bonds (N-H•••N = 2.668(2) Å, 126.1°; 2.688(2) Å, 124.6°) and are almost coplanar (angle of 8.2°) (Fig. 1). The two chelates are in a *cis* arrangement, unlike the reported analogue bearing peripheral nitrile groups.[8h] The same trend is also observed for **1a**, **2a** and **3a** (ESI).

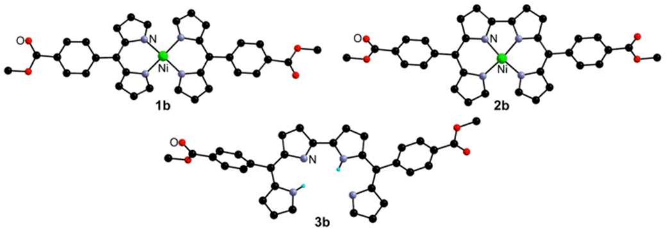

Fig. 1 Crystal structures of compounds **1b**-**3b**. CH hydrogen atoms and positional disorder are not presented for clarity.

Regarding the binuclear complexes, two 2,2′-bis-dpm ligands form a linear double helical arrangement around two Zn(II) cations separated by 3.222(2) and 3.239(5) Å for **4a** and **4b**, respectively (Fig. 2). As observed for analogous compounds,[8] the metal centers are in a distorted tetrahedral geometry with the chelates forming an angle of 59.4° in **4a** and of 53.5° and 58.3° around the two crystallographically independent Zn(II) cations in **4b** (Fig. 2). Within a ligand strand, the two dpm chelates are not coplanar and point in the same direction as demonstrated by the central NCCN torsion angle varying from 22.3 to 29.9° for **4a** and from 31.20 to 36.10° for **4b**. Both compounds crystallize in centrosymmetric space groups (ESI) and thus the racemate crystals contain complexes of *P* and *M* helicity. In the structure of the trinuclear complexes **5a** and **5b** (Fig. 1), three 2,2′-bis-dpm ligands are arranged in the over and under fashion around three metal cations defining a triangle, leading thus to a circular helicate. For both triangular complexes, the metal cations are in an environment closer to tetrahedral geometry than in the linear species with the chelates forming an angle around the metal ions varying between 66.0 and 88.3° for **5a** and between 77.2 and 79.3° for **5b** (Fig. 2). Furthermore, within a ligand strand, the two dipyrrin moieties point in opposite direction and are more coplanar than in the binuclear complexes. The central NCCN torsion angle ranges from 147.1 to 171.1° for **5a** and from 143.9 to 161.3° for **5b**. The Zn-Zn distances are much longer for the trinuclear complexes (5.959(5)-6.282(7) Å for **5a;** 6.084(4)-6.162(2) Å for **5b**) (Fig. 2), while the Zn-N distances are unaffected, when compared to **4a** and **4b**. For **6b**, four crystallographically equivalent Zn(II) cations define almost a square (Zn-Zn distance = 5.940(5), 6.159(5) Å) with four 2,2′-bis-dpm ligands wrapping around the metal ions, leading again to a circular helicate (Fig. 2). A tetrahedral coordination environment is observed with the chelates forming an angle of 80.4° around the Zn(II) ion with Zn-N distances similar to those in **4b** and **5b**. As for the triangular systems, the two chelates are oriented in opposite fashion within a bisdipyrrin strand and the central NCCN torsion angle ranges from 147.7 to 152.0°. Two types of ligands can however be identified, with the bisdipyrrin unit pointing either inwardly or outwardly from the central core of the complex (Fig. 2). Interestingly, this organization seems to be retained in solution, since two different sets of signals corresponding to the two types of ligand are observed in the ^{1}H-NMR spectrum of **6b** (ESI). In the analyzed crystals, complexes of only one helicity (either *P* or *M*) were found to be present and the whole batch was a conglomerate. Indeed, **6b** crystallizes in the chiral orthorhombic *I*222 space group and data collection on two different crystals allowed the determination of the structure of both enantiomers (ESI).

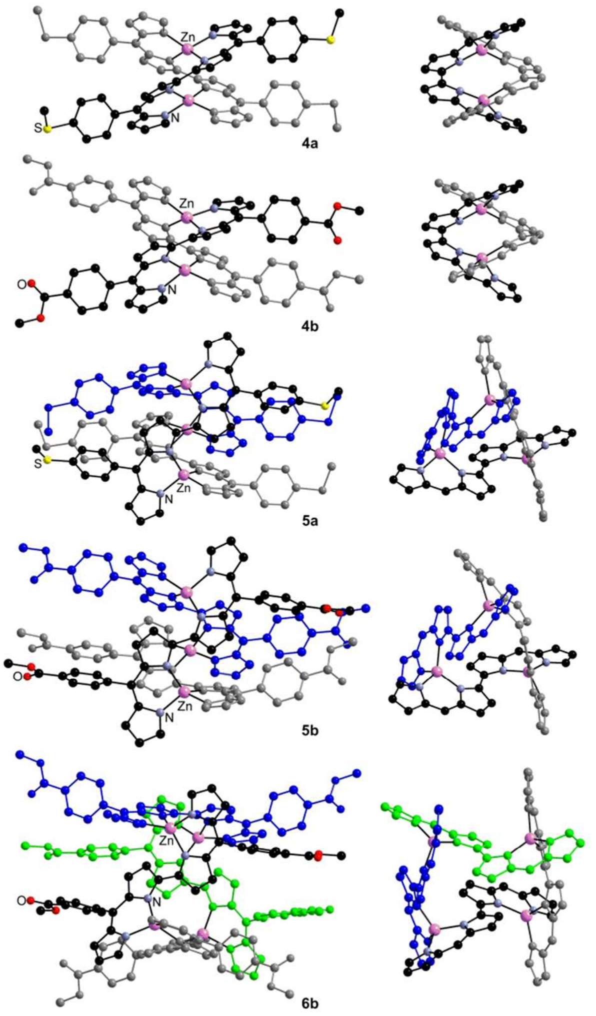

Fig. 2 Crystal structures of **4a-5a** and **4b-6b** (left) and side view of the corresponding $[Zn_x(2,2'\text{-bis-dpm})_x]$ core (x = 2, 3, 4) (right). Only the *P* helicates are presented, H atoms and solvent molecules have been omitted for clarity.

In order to investigate the behaviour and purity of these species in solution, DOSY NMR studies in CD_2Cl_2 at room temperature were performed on helicates **4b**-**6b** (ESI). In all three cases, a single species was detected in solution suggesting the absence of decomposition or interconversion between different complexes, under these conditions.

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Owing to the increase in the nuclearity of the complex from 2 to 3 and to 4 leading to an increase in the volume, one would expect a decrease in the diffusion coefficient. This was indeed the case, since the volume of the corresponding diffusing sphere was found to be twice as large for the tetranuclear complex (3680 Å^3) compared to the one obtained for the linear helicate (1640 Å^3). For the triangular helicate, an intermediate volume was determined (2500 Å^3). This is consistent with the data obtained from crystal structure determination. Furthermore, to investigate the possible interconversion between different helicates, $CDCl_3$ solutions of either **5b** or **6b** were heated at 50°C over several weeks and monitored by ^{1}H-NMR. After 10 weeks, 36 % of circular helicate **5b** was converted into **4b**. For **6b**, over the same period, only a 10 % conversion into the linear complex was detected. These observations suggest that the circular helicates are kinetic products slowly equilibrating upon prolonged heating into the binuclear thermodynamic species.

Fig. 3 presents the UV-Visible spectra of ligand **3b** and helicates **4b**-**6b** in CH_2Cl_2 solution. Upon complexation of Zn(II) cation by 2,2′-bis-dpm derivatives, a bathochromic shift is observed for the complexes in comparison with the free ligand, as for reported linear helicates.[8,14] Binuclear compound **4b** features an intense absorption band at 428 nm and two less intense bands at 583 and 635 nm (Fig. 3). Interestingly, a large increase of the molar absorptivity for the bands at lower energy is observed for both **5b** (at 614, 656, 697 nm) and **6b** (at 606, 649, 676 nm). Such a phenomenon can be related to the more stretched arrangement of the bis-dpm strands in the tri- and tetranuclear complexes leading to longer Zn-Zn distances and different relative orientation of the chelates. Indeed, based on experimental and theoretical investigations, the group of Maeda reported recently that strapped linear helicates feature a spring-like behavior with two favored modes at Zn-Zn distances around either 3.5 or 5.0 Å, resulting in modified exciton coupling between the dpm chromophores.[8f] In particular, lower energy bands were found to be enhanced for more stretched 2,2′-bis-dpm strand and hence larger distances between the metal cations.[8f] An analogous behavior seems to be at stake for **5b** and **6b**. It should also be noted that intense absorption bands at lower energy have also been described by Dolphin for Zn(II) polynuclear grids based on a fused, thus fully conjugated, 3,3′-bisdpm ligand.[7d]

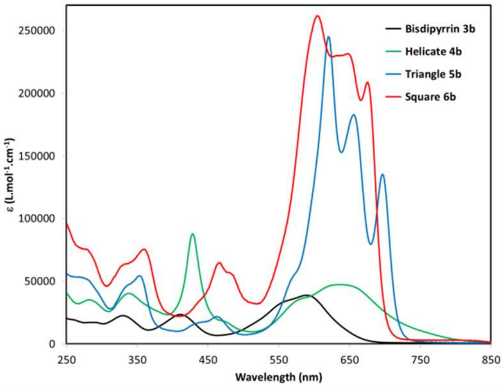

Fig. 3 Electronic absorption spectra of ligand **3b** and helicates **4b**-**6b** in CH_2Cl_2.

In conclusion, it has been demonstrated that the combination of Zn(II) cation with the 2,2′-bis-dpm based ligands **3a** and **3b**, bearing two peripheral thioether or ester groups, leads to the concomitant formation of linear and circular helicates. From the mixture of polynuclear complexes, the linear helicates **4a** and **4b** as well as triangular trinuclear circular helicates **5a** and **5b** and square tetranuclear circular helicate **6b** have been isolated and obtained as pure species. As revealed by NMR spectroscopy, all helicates generated from either **3a** or **3b** are stable in $CDCl_3$ solution at room temperature. However, upon heating the individual helicates at 50 °C in $CDCl_3$ for several weeks, the ^{1}H-NMR spectra indicated slow conversion of the circular species into the linear one. In CH_2Cl_2 solution, studies by UV-visible spectroscopy revealed a substantial enhancement of the low energy absorption bands for **5a**, **5b** and **6b**. All intermediate and final compounds have been characterized in the solid state by single-crystal X-ray diffraction. Interestingly, whereas for both triangular circular helicates **5a** and **5b**, crystals were found to be internal racemates containing both *P* and *M* helicities, the formation of a conglomerate was observed for the square circular helicate **6b**. From the batch composed of enantiomerically pure crystals, the structures of helicates of either helicity were determined. For all three circular species, the geometry around the Zn(II) cation is almost tetrahedral with longer Zn-Zn distances, when compared to the linear analogues **4a** and **4b**. This further supports the intensity enhancement observed by absorption spectroscopy. Future work will focus on the extension of this family of circular helicates to other 2,2′-bis-dpm ligands and their use for the construction of heterometallic architectures.

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Electronic Supplementary Information (ESI) available: Synthetic procedures, analytical and crystallographic data, CCDC 1040034-1040046. For ESI and crystallographic data in CIF format, see DOI: 10.1039/b000000x/

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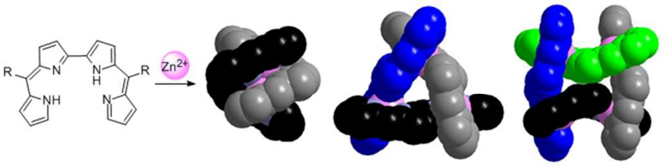
Graphical abstract

Coordination of two 2,2'-bisdipyrrin ligands, bearing either methyl ester or methylthioether peripheral groups, with Zn(II) cations leads not only to the formation of the expected linear helicates but also concomitantly to novel tri- and tetra-nuclear circular species that have been isolated and fully characterized in solution and in the solid state by single-crystal X-Ray diffraction.



Linear *vs.* circular helicates

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