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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 tetranuclear 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 extensively studied, owing to their potential application in catalysis, magnetism and optics.1-3 In particular, helicates have been widely investigated and numerous examples of linear helices have been reported.4 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.5 The vast majority of ligands employed for the preparation of such species comprises the pyridine moiety.6 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 polymers5 as well as discrete architectures,5-10 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’.10 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.

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

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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 Na2CO3 gave 2,2’-bis-dpms 3a and 3b both in 89% yield. Upon reacting overnight these ligands with one equivalent of Zn(OAc)2, in either pure CHCl3 or a CHCl3/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 CHCl3/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
performing the complexation in CH$_2$Cl$_2$/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$_2$(2,2'-bis-dpm)$_2$] and tetra-nuclear [Zn$_4$(2,2'-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 1.879(16) - 1.894(16) Å range, in agreement with a reported polymorphic structure of this compound, the distances are different (1.849(14) vs 1.894(13) Å) for 2b, as observed for other Ni(2,2'-bisdipyrrin) complexes. In the structure of ligand 3b, the two dipyrrin chelates feature intramolecular hydrogen bonds (Ni-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. The same trend is also observed for 1a, 2a and 3a (ESI).

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, 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 45.9° 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 order 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 66.3 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 171.5° for 5a and from 143.9 to 162.3° for 5b. The Zn-Zn distances are much longer for the trinuclear complexes (5.959(5)-6.282(2) 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), 6.155(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 I22z space group and data collection on two different crystals allowed the determination of the structure of both enantiomers (ESI).

In order to investigate the behaviour and purity of these species in solution, DOSY NMR studies in CD$_2$Cl$_2$ 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.
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 (368 Å³) compared to the one obtained for the linear helicate (164 Å³). For the triangular helicate, an intermediate volume was determined (250 Å³). This is consistent with the data obtained from crystal structure determination. Furthermore, to investigate the possible interconversion between different helicates, CDCl₃ solutions of either 5b or 6b were heated at 50°C over several weeks and monitored by ¹H-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 CH₂Cl₂ 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. 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. 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. 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'-bis-dpm ligand.

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 CDCl₃ solution at room temperature. However, upon heating the individual helicates at 50°C in CDCl₃ for several weeks, the ¹H-NMR spectra indicated slow conversion of the circular species into the linear one. In CH₂Cl₂ 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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**Notes and references**


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Graphical abstract

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