ChemPubSoc Europe

DOI: 10.1002/chem.201304319

CHEMISTRY
A European Journal
Communication

Coordination Polymers

A Silver Bite: Crystalline Heterometallic Architectures Based on Ag–π Interactions with a Bis-Dipyrrin Zinc Helicate

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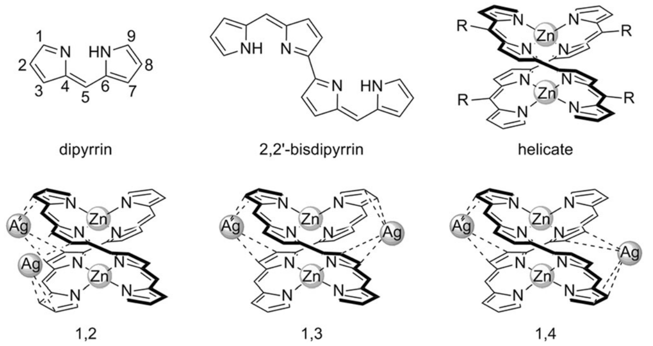
Abstract: An unprecedented mode of assembly of helical motives and Ag^I ions in the crystalline state is described. The combination of a Zn^{II} helicate based on a 2,2′-bisdpm bearing peripheral benzonitrile moieties with AgX salts, leads to the formation of a tetranuclear core containing Ag–π interactions. Depending on the coordinating ability of the X^- anion and the solvents used, the tetranuclear complex self-assembles into coordination polymers of varying dimensionality. From the sequence of coordination events (Ag–π or Ag–peripheral site), one may envisage two possible construction scenarios. However, the Ag–π as primary event seems reasonable owing to the rather weak binding propensity of the nitrile group and the chelating nature of the π-clefts.



Scheme 1. Representations of dipyrrin, 2,2′-bisdipyrrin, a Zn^{II} double helicate, and positional isomers of the heterometallic tetranuclear Ag_2Zn_2 species.

Over the past decade, the sequential approach for the construction of heterometallic coordination polymers (CPs) and metal–organic frameworks (MOFs), relying on the use of ligands bearing differentiated coordination poles, has demonstrated its efficiency.[1] In this strategy, coordination of a first metal center leads to the formation of a discrete complex bearing peripheral binding sites which may be regarded as a metallatecton.[1,2] The latter leads in the presence of a second metal cation to a self-assembled heterometallic periodic architecture. Although, following this strategy, a variety of ligands has been employed, the bis-pyrrolic derivatives of the dipyrrin type (dpm) appeared as particularly appealing.[3] Indeed, not only the dpm moiety forms a monoanionic chelate under mild basic conditions, but its straightforward functionalization at position 5 by an additional peripheral coordinating site leads to a family of differentiated ligands (Scheme 1). Using this type of multipole ligand, several dpm-based heterometallic CPs have been described, in particular with Ag^I as the secondary metal center.[4,5] In some of these architectures, the Ag^I ion is found to form Ag–π interactions[6] with C=C bonds of the dpm chelate, in addition to the expected classical binding to the peripheral coordinating pole.[5] Whereas this interaction has been documented with aromatic compounds,[6] its observation in the solid state with pyrrolic systems remains rather rare.[5,7] In solution, it has been investigated with tetrapyrrolic derivatives such as 3,3′-bisdipyrrin helicates and Ce(IV) double-decker porphyrins.[8,9] In the latter type of compounds, two pyrrolic rings of facing macrocycles form π-clefts interacting with Ag^I ions, as determined by NMR, Raman, and UV/Vis spectroscopies.[9] Based on our previous investigations on Ag–π interactions in the crystalline phase,[5] it appeared interesting to exploit this type of interaction as a construction strategy for the generation of extended heterometallic architectures. Such an approach requires the design of metallatectons incorporating both π-clefts and peripheral coordinating sites. Interestingly, bis- and oligo-pyrrolic ligands[10] have been shown to form helicates with Zn^{II} ions.[11] In particular, the 2,2′-bisdipyrrin Zn^{II} double helicate (Scheme 1) displays four π-clefts formed by pyrrolic rings of two different strands. Owing to the proper disposition and distances between the π-bonds, such a helicate should behave as a silver binder through Ag–π interaction leading thus to three tetranuclear Ag_2Zn_2 heterometallic positional isomers (Scheme 1). Upon introducing two peripheral coordinating sites at both positions 5 on the 2,2′-bisdipyrrin backbone, the binuclear silver Zn^{II} helicate should behave as a self-complementary metallatecton displaying simultaneously four coordinating sites and two secondary metal centers offering free coordination sites. The latter, in principle, should self-assemble into CPs upon coordination of the peripheral binding units to the Ag^I centers. Although helicate type complexes have been investigated with a variety of organic ligands and metals,[12] only very few have been employed as metallatectons

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201304319.

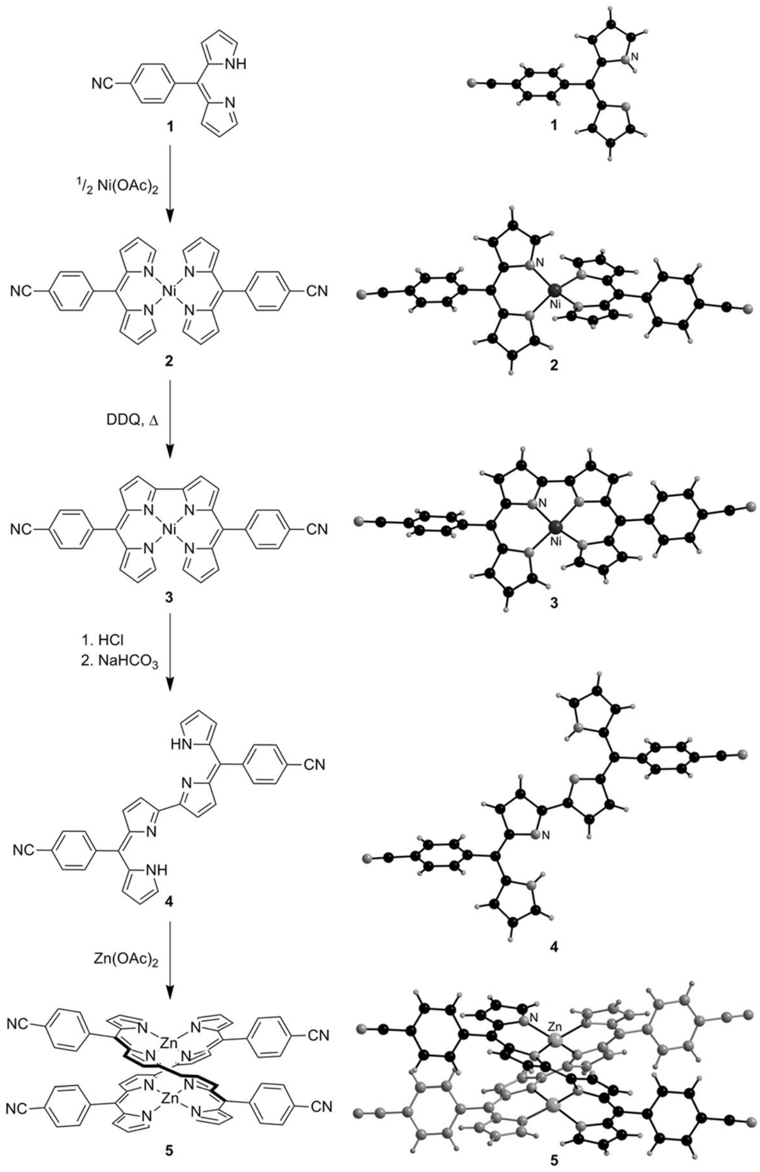

Figure 1. Synthetic pathway for the preparation of helicate **5** (left) and crystal structures of compounds **1**–**5** (right).

for the preparation of heterometallic CPs using classical coordination bonds.[13]

We report herein that, upon combining the Zn^{II} helicate based on a 2,2′-bisdpm bearing peripheral benzonitrile moieties (Complex **5**, Figure 1) with AgX salts, a tetranuclear core is formed by Ag–π interactions. The latter, depending on the nature of the anion X^- and the solvents used, leads to 0-, 1-, 2-, or 3D heterometallic architectures.

The synthetic scheme for the preparation of the target metallatecton **5** is presented in Figure 1 (for experimental details see the Supporting Information). The Ni-templated method as reported by Scott was used for the synthesis of bis-dipyrrin **4**.[14] Reaction of the benzonitrile-appended dipyrrin **1**[15] with $Ni(OAc)_2$ afforded complex **2** in 50% yield.[16] Subsequent oxidation by DDQ followed by demetallation using HCl led to the formation of complex **3** and bis-dipyrrin **4** in 65 and 80% yield respectively. Reaction of the latter with $Zn(OAc)_2$ afforded quantitatively the helicate **5**.

The crystal structures of all five compounds **1**–**5** determined by X-Ray diffraction (Table S1 in the Supporting Information) are given in Figure 1. For **1**, the two pyrrolic rings are almost coplanar, owing to the presence of an intramolecular hydrogen bond (N–H–N = 2.716(3) Å, 124.6°) as observed for other dipyrrins.[17] The Ni^{II} ion in **2** is coordinated to two dpm chelates in a pseudo-tetrahedral environment with Ni–N distances ranging from 1.889(3) to 1.906(3) Å (Figure 1), as expected for such compound.[16,18] Upon oxidation leading to the formation of a bond between the two chelates (**3**), the Ni^{II} ion adopts a distorted square planar environment (Figure 1). This planarization of the complex is apparent when comparing the angle between the two dpm moieties, 53.1 vs. 20.3° for **2** and **3**, respectively. However, complex **3** is not flat but helical, as a result of the repulsion between the two remaining αC–Hs, with both *P* and *M* helices present in the crystal. Owing to the strain resulting from the formation of the bis-dpm ligand, two Ni–N distances are shorter than the others (1.8527(14) and 1.8582(14) vs. 1.8920(15) and 1.8979(14) Å), as described for similar complexes.[19] For the free 2,2′-bisdpm ligand **4** (Figure 1), the four pyrrolic rings are almost coplanar and, as for **1**, an intramolecular hydrogen bond is observed within the dpm (N–H–N = 2.758(3) Å, 122.1°). For **5**, the two bisdpm strands are arranged into a double helix maintained by the two Zn^{II} ions (Figure 1). Again, the crystal is a racemate containing both *P* and *M* helices. The Zn^{II} centers, distant of 3.287 Å, are in a distorted tetrahedral coordination environment with the two dpm chelates forming an angle of 56.0 and 57.5°.[11] Within a strand, the two dipyrrin moieties are tilted by 48.7 and 55.3°.

In order to investigate the formation of the tetranuclear Ag_2Zn_2 helical species as well as the role played by the anion X^- and by the solvent, the binuclear Zn^{II} helicate **5** in $CHCl_3$ or CH_2Cl_2 was combined with AgX salts ($X^- = TfO^-$, BF_4^-, and SbF_6^-) in THF or AcOEt. Single crystals of the heterometallic architectures **6**–**10** were thus obtained after few weeks and studied by X-ray diffraction on single crystals.

In the case of TfO^-, upon slow diffusion of a THF solution of Ag(TfO) into a $CHCl_3$ solution of **5**, the discrete tetranuclear complex **6**, $\{(\mathbf{5})[(Ag(TfO)(THF)]_2\}(CHCl_3)_2$ was obtained. As predicted, the crystal structure of **6** (monoclinic, *C*2/*c*) revealed that two Ag^I ions are complexed by the helicate **5** through Ag–π interactions with two pyrrolic ring belonging to a π-cleft (Figure 2). The Ag–C distances, ranging from 2.469(3) to 2.588(3) Å, are similar to those observed with mono-dpm based metallatectons.[5] The coordination sphere of Ag^+ ion is completed by a TfO^- anion and a THF molecule. Interestingly, none of the peripheral nitrile groups are coordinated to the Ag^I centers, leading thus to a discrete complex. While three po-

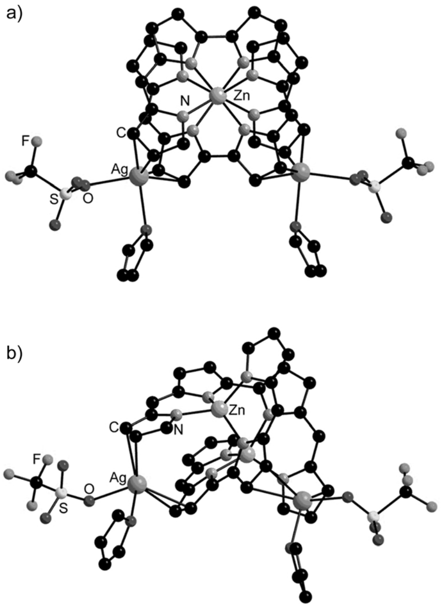

Figure 2. a) Top and b) side views of the tetranuclear complex in the structure of **6**. Hydrogen atoms, $CHCl_3$ solvent molecules, and benzonitrile groups have been omitted for clarity. Note that only one of the two positions of the disordered THF is presented.

sitional isomers may be expected for **6** (Scheme 1), the structural study revealed only the presence of the 1,4 isomer (Figure 2). Furthermore, the crystal is a racemate containing both *P* and *M* helicates. This discrete complex was also characterized by mass spectrometry showing signals corresponding to the helicate as well as the trinuclear complex $[(\mathbf{5})\mathrm{Ag}]^+$ (Figure S8 in the Supporting Information). In addition, ^{1}H NMR investigation revealed that, in [D$_8$]THF solution, the decomplexation of the Ag$^\mathrm{I}$ ions occurs, since only the spectrum of the free helicate **5** was observed.

In order to avoid the binding of THF by Ag$^+$ ion, as observed for **6**, and thus generate extended networks, AcOEt was used instead. Upon diffusion of a AcOEt solution of Ag(TfO) in a CH_2Cl_2 solution of **5**, crystals (triclinic, $P\bar{1}$) of the network **7**, $\{(\mathbf{5})[(\mathrm{Ag(TfO)}]_2\}_\infty(\mathrm{CH_2Cl_2})_3$, were obtained. As for **6**, again the 1,4 isomer of the tetranuclear complex (Figure 3) with Ag–C distances ranging from 2.393(3) to 2.692(3) Å is formed. Compounds **6** and **7** differ by the coordination sphere of the two Ag$^+$ ions. Indeed, for **7**, the two crystallographically independent Ag$^\mathrm{I}$ centers are both coordinated to a bridging triflate anion, but their surrounding differs by the presence of either a peripheral CN group of a neighboring helicate (Ag–N = 2.304(3) Å) or of a terminal TfO$^-$ anion. This leads to the formation of a 1D network comprising both *P* and *M* helices (Figure 3). As anticipated, the replacement of THF by AcOEt leads to the self-assembly of the tetranuclear core into a coordination polymer through binding of the secondary metal centers by the peripheral nitrile group.

It is worth noting that the synthesis of **7** also leads to the formation of crystals of network **8**, $\{(\mathbf{5})\mathrm{Ag}_2\}_\infty(\mathrm{TfO})_2(\mathrm{CH_2Cl_2})$ (Triclinic, $P\bar{1}$). For the latter, again the same type of tetranuclear motif based on Ag–π interactions as the one observed for **6** and **7** is formed with similar Ag–C distances ranging from 2.420(4) to 2.688(4) Å. However, the 1,3 isomer is present here. Furthermore, the triflate anions are not anymore bound to the Ag$^\mathrm{I}$ centers (Figure 4). Instead, the two Ag$^\mathrm{I}$ ions are coordinated to two nitrile groups of neighboring helicates (Ag–N = 2.253(4) to 2.392(4) Å), leading thus to a 2D CP with alternating *P* and *M* helicity (Figure 4).

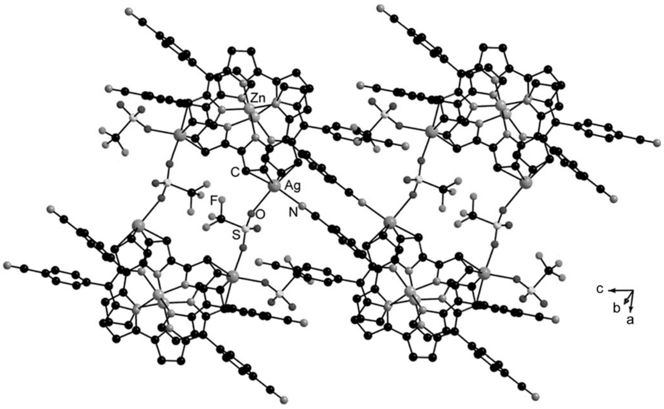

Figure 3. Portion of the 1D network in the structure of **7**. Hydrogen atoms and CH_2Cl_2 molecules have been omitted for clarity. Note that only one position of the disordered bridging triflate anion is presented.

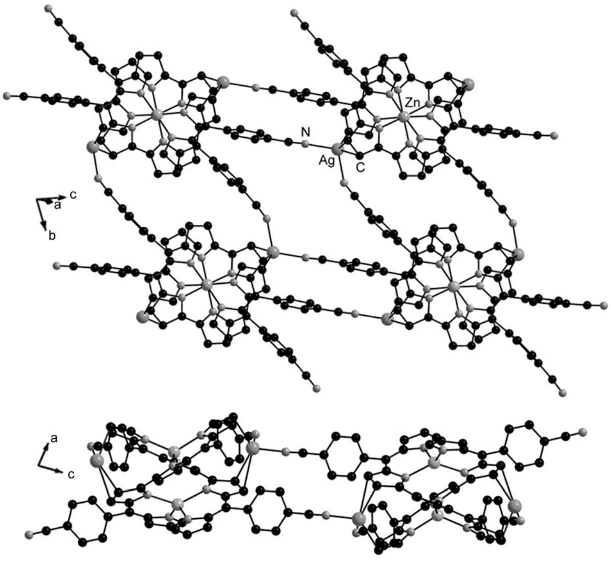

Figure 4. Top and side views of portions of the 2D network in **8**. Hydrogen atoms, anions, and solvent molecules have been omitted for clarity. Note that only one position of the one disordered Ag$^\mathrm{I}$ ion is presented.

In order to investigate the role played by the anion on the assembly process, a THF solution of AgX was diffused into a $CHCl_3$ solution of **5**, affording crystals of the coordination polymers $\{(\mathbf{5})\mathrm{Ag}_2\}_\infty(\mathrm{X})_2$ (X$^-$ = BF_4^-, **9**; SbF_6^-, **10**). For both isomorphous racemic crystals (monoclinic, *C*2/*c*), the 1,3 positional isomer of the tetranuclear core $\{(\mathbf{5})\mathrm{Ag}_2\}^{2+}$ self-assembles into a 3D network. The formation of the latter results from mutual interconnection of consecutive helical tetranuclear moieties through CN–Ag bonds (Figure 5). The 3D network is porous with cavities occupied by anions as well as by solvent mole-

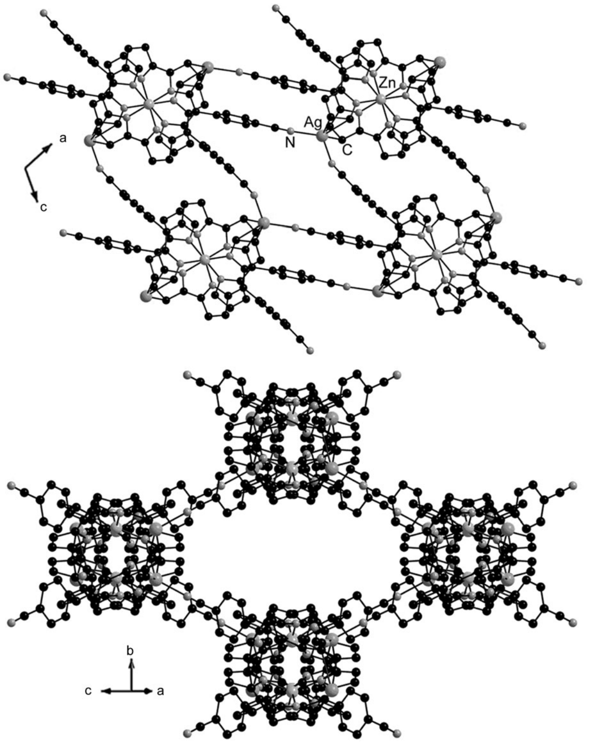

Figure 5. Top and side view of the 3D network in **9**. Hydrogen atoms and anions have been omitted for clarity.

cules. However, the latter showed important positional disorder and the SQUEEZE command was applied to refine the structure.[20]

In conclusion, in order to take advantage of robust Ag–π interactions in the crystalline phase, the benzonitrile appended Zn^{II} helicate **5** displaying both π-clefts and peripheral coordinating sites was designed and prepared. Its combination with AgX salts shows the recurrent formation of a tetranuclear Ag_2Zn_2 double helical core resulting from Ag–π interactions. Depending on the coordinating ability of X^- anion and the solvents used, the tetranuclear complex self-assembles into coordination polymers of varying dimensionality. Although, depending on the sequence of coordination events (Ag–π or Ag–peripheral site), one may envisage two possible construction scenarios, the Ag–π as primary event seems reasonable owing to the rather weak binding propensity of the nitrile group and the chelating nature of the π-clefts. This is further supported by the formation of the discrete complex **6**. It is worth noting that the viable design principle reported purposely combines three distinct binding modes (chelate Zn-dpm, Ag-π-cleft, Ag–NC). The foregoing results not only illustrate an unprecedented mode of assembly of helical motives and Ag^{I} ions in the crystalline state, but also represent rare examples of the use of helicates as metallatectons for the construction of heterometallic coordination polymers. Current investigation in our laboratory focuses on the use of this motif with other helicates.

Experimental Section

Experimental details for the synthesis of **3**--**10** as well as analytical data and Figures S1–S5 in color are available in the Supporting Information. CCDC-963114 (**1**), CCDC-963115 (**2**), CCDC-963116 (**3**), CCDC-963117 (**4**), CCDC-963118 (**5**), CCDC-963119 (**6**), CCDC-963120 (**7**), CCDC-963121 (**8**), CCDC-963122 (**9**), and CCDC-963123 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the Université de Strasbourg, the Institut Universitaire de France, the International centre for Frontier Research in Chemistry (icFRC), CONACYT, the CNRS, and the Ministère de l'Enseignement Supérieur et de la Recherche for financial support.

Keywords: Ag–π interactions · helicates · molecular tectonics · self-assembly · silver

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Received: November 4, 2013