

Communication

Hydrogen Bonding Directed Self-Assembly of a Binuclear Ag(I) Metallacycle into a 1D Supramolecular Polymer

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Abstract: An Ag(I) metallacycle obtained unexpectedly during the preparation of Pd(II) complexes of the bifunctional ligand 5-([2,2'-bipyridin]-5-yl)pyrimidine-2-amine (**L**) has been characterized using X-ray structure determination as a binuclear, metallacyclic species [Ag₂L₂](SbF₆)₂, where both the bipyridine and pyrimidine-N donors of **L** are involved in coordination to the metal. The full coordination environment of the Ag(I) defines a case of highly irregular 4-coordination. In the crystal, the Ag-metallacycles assemble into one-dimensional supramolecular metalladynamers linked together by hydrogen-bonding interactions.

Keywords: supramolecular chemistry; metalladynamers; H-bond polymers; metallacycles

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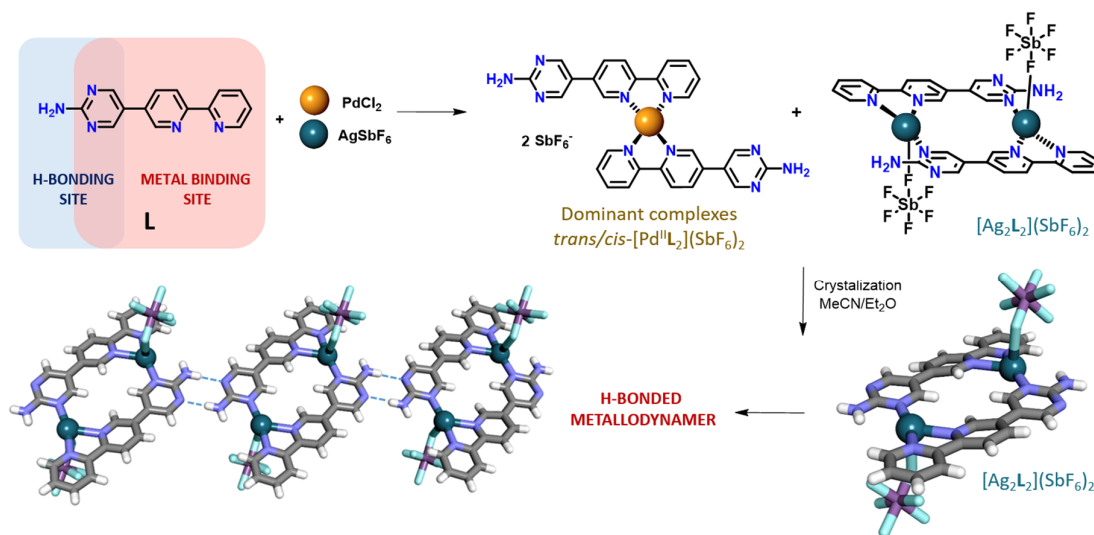
1. Introduction

In the last three decades, a great deal of effort has been devoted to the preparation and further investigation of metallosupramolecular assemblies in the solid state, because they not only extend the range of new structures, which can be designed to possess particular physical and chemical properties but often lead to unexpected applications of such materials [1–3]. In this context, the control of the self-assembly process between labile metal ions and multidentate ligands is a key objective in the development of new metallosupramolecular materials based on the simultaneous use of distinct dynamic linkages [4–6]. Clearly, this process is related to a variety of factors, such as the number, type, and spatial disposition of the binding sites of ligands; the stereoelectronic preferences of metal ions; the solvent used; and the nature of counter ions. [7,8]. The combination of all of these factors leads to numerous metallosupramolecular complexes with various structural topologies and fascinating physicochemical properties [9–15].

Among the various types of supramolecular linkages employed in the generation of complex assemblies, coordination and hydrogen bonds are the most widely employed [16–21]. It is worth noting that despite the incredible progress made in this area of chemistry in recent years, the simultaneous application of both these bonds for the generation of topologically non-trivial supramolecular architectures remains challenging, especially with the use of highly labile metal ions, such as Ag(I) [22–26]. In fact, little attention has been paid to the generation of supramolecular assemblies produced by means of simultaneous hydrogen and coordination bonding with Ag(I) as their metal centers [27–29]. Ag(I) is an interesting metal, with several coordination geometries having been described, such as linear [30], T-shaped [31], trigonal [32], distorted tetrahedral [33], and octahedral geometries [34], and each particular geometry is usually a consequence of the coordination

properties of the ligands [35]. In this context, the application of this labile metal ion with a ligand containing two distinct chelating groups—i.e., pyrimidine and bipyridine—with an additional functional moiety promoting hydrogen bonds remains unexplored.

The bifunctional ligand 5-([2,2'-bipyridin]-5-yl)pyrimidin-2-amine, **L** (Scheme 1), contains both a strong chelation site of the 2,2'-bipyridine type and a strong H-bond acceptor–donor (ADDA) site, a combination anticipated to be of particular utility in the supramolecular chemistry of metal ion complexes. We have shown that with the octahedral metal ion Fe(II) [36], it is possible to isolate both the *meridional* and *facial* forms of its tris(ligand) complexes, in which only the bipyridine site is directly bound to the metal and the aminopyrimidine unit is free to become involved in supramolecular interactions which differ greatly for the two isomers. In contemplating extension of this work to metal ions with different coordination preferences, our first choice was that of a square-planar Pd(II), one of the most versatile and widely used sources of efficient metallocatalysts [37–41]. Again (Scheme 1), it was expected that two isomers, here *cis* and *trans*, might form and that fractional crystallization might be required in their separation. In the event, fractional crystallization of the product mixture obtained by reacting Pd(SbF₆)₂, obtained in situ by reacting PdCl₂ with AgSbF₆ in aqueous acetonitrile, with **L** did produce two distinct materials, the first a poorly crystalline mixture of the Pd(II) complexes and the second being the unexpected Ag(I)-based metallocycle, [Ag₂L₂](SbF₆)₂. We have also found that isolated Ag(I) complex, self-assembles in the solid state and forms extended 1D supramolecular polymer, consisting of macrocyclic monomers linked together by means of H-bonding interactions.



Scheme 1. Anticipated synthesis of the *cis* and *trans* isomers of [Pd^{II}L₂](SbF₆)₂ accompanied by the inadvertent formation of [Ag₂L₂](SbF₆)₂.

2. Results

While the reaction of Pd(SbF₆)₂ with the ligand **L**, 5-([2,2'-bipyridin]-5'-yl) pyrimidin-2-amine does indeed give rise to isomeric forms of the complex [PdL₂]²⁺ (Scheme 1; work to be reported elsewhere), on the very first occasion that it was conducted an apparent excess (0.1 equiv.) of AgSbF₆ in the reaction mixture led to these isomers being produced along with the Ag(I) complex.

Thus, a suspension of the ligand in CH₃CN was mixed at room temperature with a CH₃CN:H₂O (1:1) solution of Pd(SbF₆)₂, generated in situ from PdCl₂ and AgSbF₆, and stirred until a clear yellow solution had formed. As the color appeared consistent with the binding of the bipyridine unit to Pd(II), ESI-MS analysis (Supplementary Figures S3 and S4 in ESI) showed a dominant peak for the ion [Pd^{II}L₂(SbF₆)]⁺ the solution was evaporated

to dryness and the residue redissolved in pure CH_3CN . A vapor diffusion of diethylether into this solution with the intention of isolating the $[\text{Pd}^{\text{II}}\text{L}_2](\text{SbF}_6)_2$ presumed to be present initially provided poorly crystalline material, but on removing this and allowing the supernatant to evaporate slowly, small, pale-yellow crystals were obtained. These proved to be almost completely insoluble in any solvent, indicating that the species originally formed in CH_3CN was no longer present. The exact nature of this material was established by X-ray structure determination (and subsequent chemistry). Thus, the isolated crystalline complex proved not to be a chelate complex of Pd(II) but a diargentacycle, $[\text{bis}[5 - ([2',2''\text{-bipyridin}] - 5'\text{-yl})\text{pyrimidin-2-amine}]]\text{disilver(I)} \text{ bis}(\text{hexafluoroantimonate})$, $[\text{Ag}_2\text{L}_2](\text{SbF}_6)_2$, involving Ag(I) in a four-coordinate environment provided by not only the two N-donors of the bipyridine unit but also by one pyrimidine-N and one fluorine of $[\text{SbF}_6]^-$ (Figure 1a). The crystal and structure refinement data for this complex are given in Table 1. Unlike the Fe(II) complexes of **L**, the ligand here acts as a triple N-donor by bridging the two Ag(I) centers. The binuclear complex unit is centrosymmetric, with Ag-N bond lengths which vary significantly—namely, Ag1-N3 2.151(10); Ag1-N4 2.385(10); and Ag1-N5 2.217(10) Å—covering a range similar to that of the known $[\text{Ag}(2,2'\text{-bipyridine})_2]^+$ species [42]. Within the diargentacycle unit, the Ag...Ag separation is 7.879(2) Å and while there is a shorter separation of 4.862(2) Å between Ag centers in adjacent diargentacycles (Figure 1b), both clearly indicate a lack of metal-metal interactions..

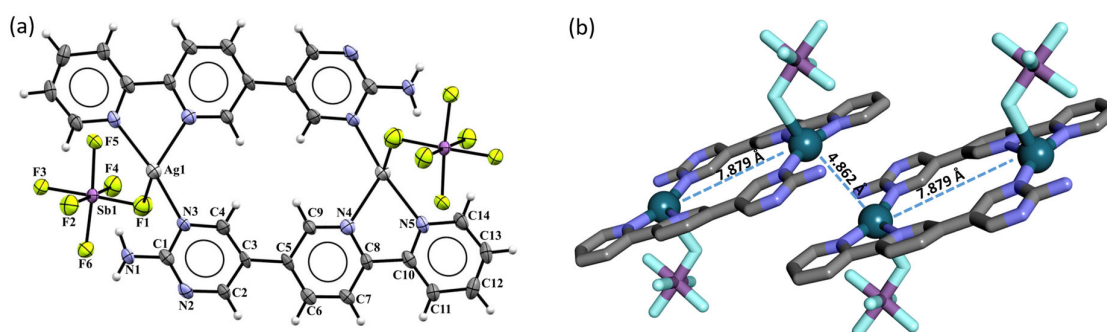


Figure 1. (a) ORTEP representation of the stoichiometric unit of $[\text{Ag}_2\text{L}_2](\text{SbF}_6)_2$ (Ag1-N3 2.151(10); Ag1-N4 2.385(10); and Ag1-N5 2.217(10) Å). Atom numbering is given for the asymmetric unit and the displacement probability ellipsoids are shown at the 50% level, (b) Ag...Ag separations within one molecule and between adjacent molecules (H-atoms have been omitted for clarity).

Table 1. Crystal and structure refinement data for $[\text{Ag}_2\text{L}_2](\text{SbF}_6)_2$.

| Chemical Formula | $\text{C}_{28}\text{H}_{22}\text{F}_{12}\text{N}_{10}\text{Ag}_2\text{Sb}_2$ |
|------------------------------------|--|
| Formula weight/g mol ⁻¹ | 1182.85 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 8.7047(2) |
| b/Å | 10.6721(3) |
| c/Å | 18.4607(5) |
| $\alpha/^\circ$ | 90 |
| $\beta/^\circ$ | 103.255(3) |
| $\gamma/^\circ$ | 90 |
| V/Å ³ | 1669.26(8) |
| Z | 2 |
| 2 Θ Range/ $^\circ$ | 9.638–151.172 |
| | h = −10→10 |
| Index ranges | k = 0→12 |
| | l = 0→23 |
| D _x /g cm ⁻³ | 2.359 |
| μ/mm^{-1} | 22.961 |

| | |
|-----------------------------------|----------|
| Temperature/K | 100.0(1) |
| F(000) | 1128.0 |
| Reflections collected | 3325 |
| Independent reflections | 3325 |
| Reflections with $I > 2\sigma(I)$ | 2955 |
| R_{int} | merged |
| Number of refined parameters | 246 |
| $R[F^2 > 2\sigma(F^2)]$ | 0.065 |
| $wR(F^2)$ | 0.191 |

Silver(I) is somewhat notorious for its variety of coordination numbers and the irregularity of its coordination sphere [43], and the present complex provides further examples. The coordination geometry is very irregular, with the Ag displaced only slightly (0.209 (2) Å) from the plane of the three N-donors, but the bond angles N3-Ag1-N4 120.9°, N3-Ag1-N5 161.8°, and N4-Ag1-N5 72.5° are very far from those for a trigonal environment. The displacement of Ag is clearly towards the fourth donor atom provided by the [SbF₆]⁻. One NH atom does lie close to what might be considered a coordination site, which would give the Ag a nearly square-planar N₃H environment, but the estimated Ag...H distance of 2.7 Å seems too long for any agostic interaction [44] to be significant.

While there are different forms of coordination of the ligand L to Ag(I) and Fe(II), the complexes of [Ag₂L₂](SbF₆)₂ and *mer*-[Fe^{II}L₃](BF₄)₂·9H₂O [36] in the solid state share a common mode of interaction involving the amino-pyrimidine units, where just half of the capacity of one unit, as ADDA H-bonding entities, is used in the formation of single-strand polymers (Figure 2).

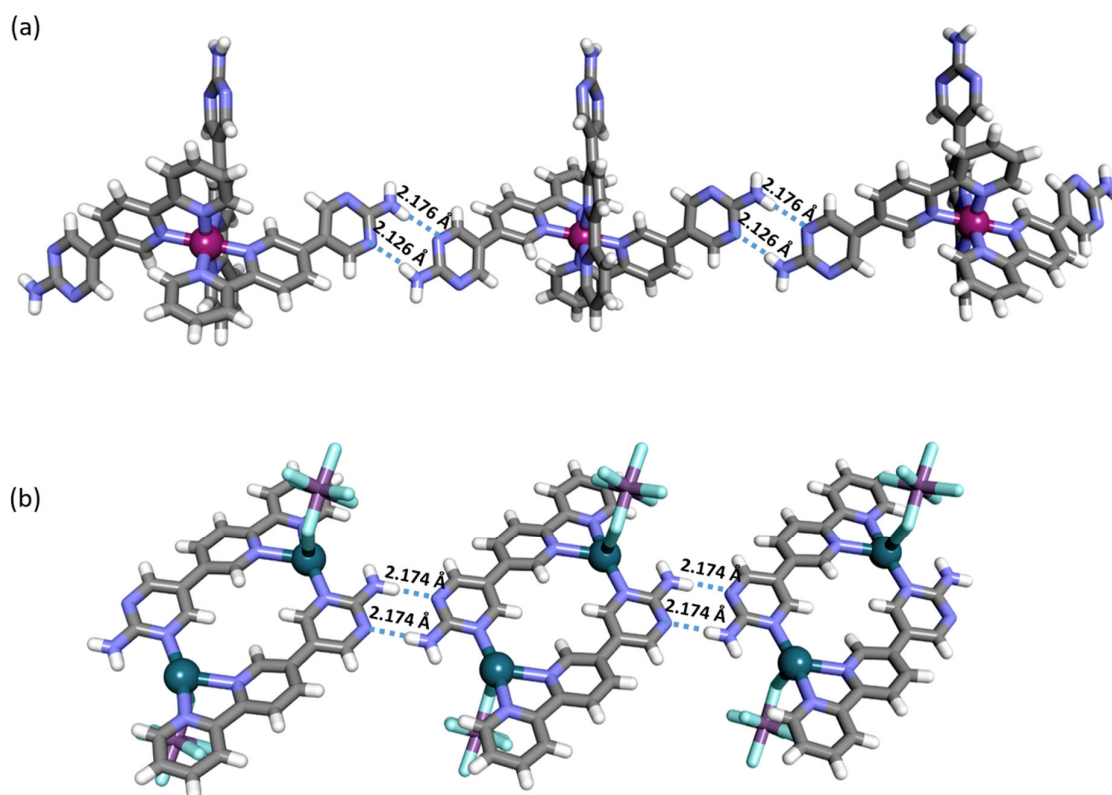


Figure 2. (a) Portion of the polymer formed by the [Fe^{II}L₃](BF₄)₂·9H₂O, (b) portion of the polymer formed by the [Ag₂L₂](SbF₆)₂.

In the silver complex structure, two independent single-stranded H-bond polymer units can be observed, running along the $[110]$ and $[1\bar{1}0]$ crystallographic directions (Figure 3). These strands are cross linked by the multiple $F\cdots HN$ and $F\cdots HC$ interactions of the $[SbF_6]^-$ units in addition to their coordination to $Ag(I)$, all evident on the Hirshfeld surface [45] (calculated using CrystalExplorer) [46] of the anion formally present. A full listing of the H-bonding interactions within the structure of $[Ag_2L_2](SbF_6)_2$ is given in Table 2. Unlike the structure of $mer-[FeIII_3](BF_4)_2\cdot 9H_2O$, that of $[Ag_2L_2](SbF_6)_2$ shows no evidence of significant apparent void space (Figure S6).

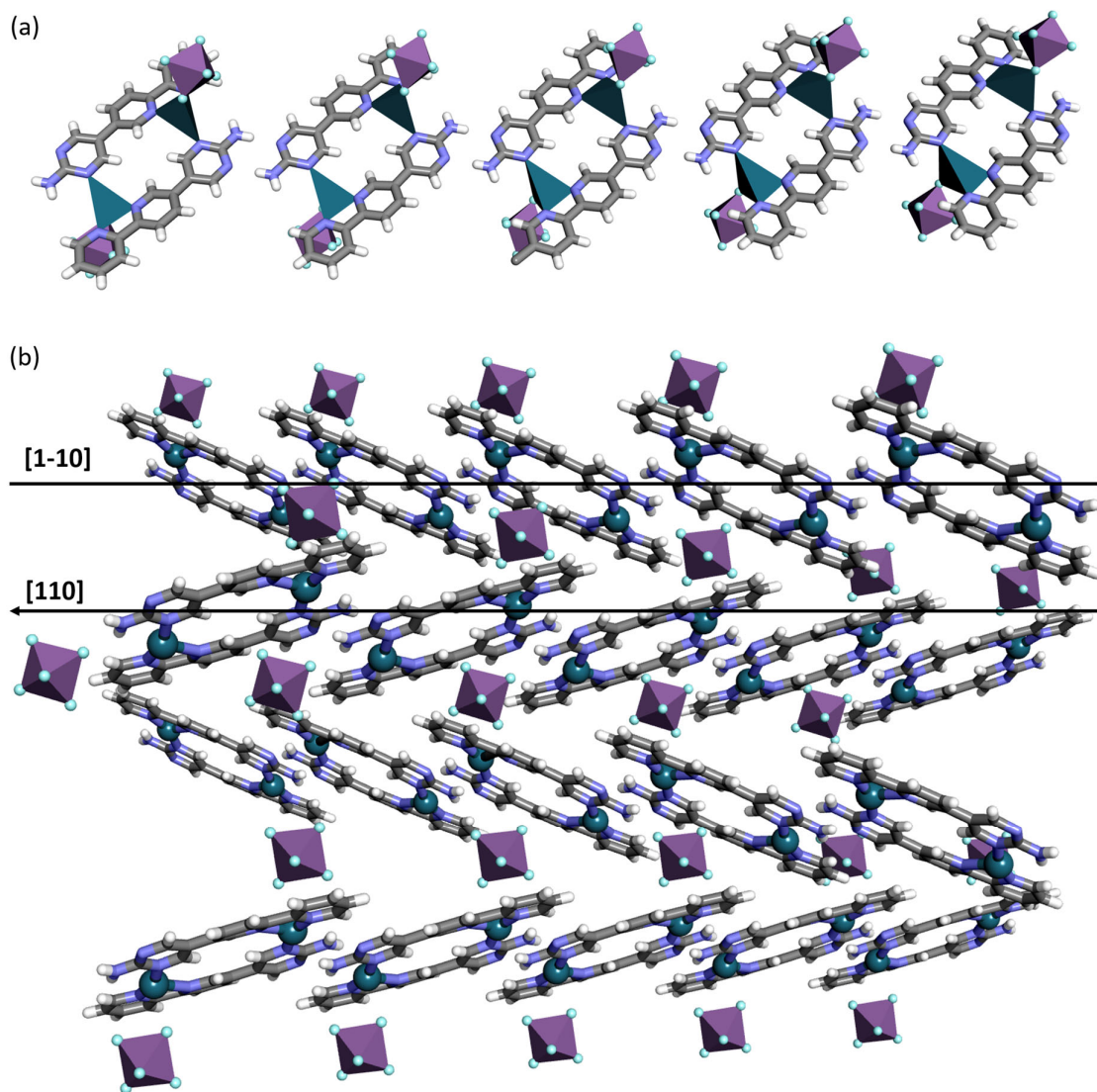


Figure 3. (a) Single-stranded H-bonded polymer system; (b) the lattice, viewed along the $[100]$ direction, showing adjacent non-covalently linked polymer systems running along the $[110]$ and $[1\bar{1}0]$ directions.

Table 2. Hydrogen bond geometry in $[Ag_2L_2](SbF_6)_2$.

| $D-H\cdots A$ | $D-H$ [Å] | $H\cdots A$ [Å] | $D\cdots A$ [Å] | $D-H\cdots A$ [°] |
|------------------------------------|-----------|-----------------|-----------------|-------------------|
| $C9-H9\cdots F3$ ⁱⁱ | 0.95 | 2.69 | 3.558 (14) | 152 |
| $N1-H1A\cdots N2$ ⁱⁱⁱ | 0.81 | 2.17 | 2.954 (13) | 163 |
| $N1-H1B\cdots F4$ ^{iv} | 0.88 | 2.37 | 2.914 (13) | 120 |
| $C12-H12\cdots F5$ ^{viii} | 0.95 | 2.84 | 3.452 (14) | 123 |
| $C11-H11\cdots F6$ ^{vii} | 0.95 | 2.56 | 3.147 (14) | 120 |

| | | | | |
|----------------------------|------|------|------------|-----|
| C6—H6...F5 ^v | 0.95 | 2.64 | 3.264 (12) | 124 |
| C6—H6...F3 ^v | 0.95 | 2.45 | 3.364 (13) | 162 |
| C13—H13...F6 ^{vi} | 0.95 | 2.72 | 3.307 (15) | 121 |
| C14—H14...F6 ^{vi} | 0.95 | 2.58 | 3.250 (13) | 128 |
| C14—H14...F4 ^{vi} | 0.95 | 2.57 | 3.507 (15) | 170 |
| C2—H2...F5 ^v | 0.95 | 2.47 | 3.301 (13) | 146 |

Symmetry codes: (ii) $x - 1/2, -y + 3/2, z - 1/2$; (iii) $-x + 1, -y + 2, -z + 1$; (iv) $-x + 1/2, y + 1/2, -z + 3/2$; (v) $x + 1/2, -y + 3/2, z - 1/2$; (vi) $x - 1/2, -y + 1/2, z - 1/2$; (vii) $-x + 1, -y + 1, -z + 1$; (viii) $x + 1/2, -y + 1/2, z - 1/2$.

3. Materials and Methods

3.1. General Methods

Basic chemicals and solvents were purchased from commercial sources and were used without further purification. The ^1H NMR spectra were acquired on Bruker Fourier 300 or 600 spectrometers equipped with a ^1H 5 mm probe and referenced to the solvent residual peaks ($\text{CD}_3\text{CN}/\text{D}_2\text{O}$, $\text{DMSO}-d_6$). NMR solvents were purchased from Deutero GmbH (Kastellaun, Germany) and used as received. The ESI-MS spectra were recorded on a Bruker Impact HD Q-TOF spectrometer in the positive ion mode. Powder X-ray diffraction patterns (PXRD) were recorded on a BRUKER D8-Focus Bragg–Brentano X-ray powder diffractometer equipped with a Cu sealed tube ($\lambda = 1.54178 \text{ \AA}$) at room temperature. Experimental and calculated powder patterns from the crystal structures were analyzed using the Kdif software [47].

3.2. Details of the Crystal Structure Solution and Refinement

Single-crystal diffraction data for the $[\text{Ag}_2\text{L}_2](\text{SbF}_6)_2$ were collected on a Rigaku XtaLAB Synergy-R diffractometer with a rotating anode using a $\text{CuK}\alpha$ radiation source ($\lambda = 1.54184 \text{ \AA}$). The low temperature was achieved using the Cryostream cooling system. Data collection and data reduction were performed using the CrysAlis PRO software [48]. The structure was solved and refined using SHELXT-2015 (intrinsic phasing method) and SHELXL-2015 (least-squares method), respectively [49,50]. Olex2 provided the support for the full structural analysis of the complex [51]. A twin matrix $-1 \ 0 \ 0 \ 0 \ -1 \ 0 \ 0.973 \ 0 \ 1$, which corresponds to a 180° rotation about the (001) reciprocal lattice direction, was also determined using the Olex2 software. The measured crystal was identified as a non-merohedral twin. The refinement process was performed using the diffraction data written in the HKLF 5 format. The BASF parameter was refined at 0.0964(17). All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were positioned geometrically in their calculated positions and refined using the riding hydrogen model.

3.3. Experimental Data for the Complex $[\text{Pd}^{\text{II}}\text{L}_2](\text{SbF}_6)_2$

The complex (bis[5-([2,2'-bipyridin]-5-yl)pyrimidin-2-amine]-palladium(I) bis(hexafluoroantimonate)- $[\text{Pd}^{\text{II}}\text{L}_2](\text{SbF}_6)_2$ was prepared using simple procedures, analogous to those used to obtain the iron(II) complex [36]. A suspension of the ligand L (25.0 mg, 0.1 mmol, 2.00 equiv.) in MeCN (5 mL), was stirred for 10 min at room temperature.

Then, the $\text{Pd}(\text{SbF}_6)_2$ salt was prepared by mixing PdCl_2 (0.05 mmol, 1 equivalent) dissolved in 2.5 mL of MeCN, and AgSbF_6 (0.105 mmol, 2.1 equivalent) dissolved in 2.5 mL of H_2O . The mixture was stirred for 15 min at room temperature and then filtered through a syringe filter. This freshly generated $\text{Pd}(\text{SbF}_6)_2$ (0.05 mmol, 1.00 equivalent) was added to the ligand in the CH_3CN and the resulting clear yellow solution was stirred at room temperature for 30 min. The solution was then evaporated to dryness under reduced pressure and the residue redissolved in MeCN (1 mL). The addition of diethylether (10 mL) produced a pale-yellow precipitate, which was collected by centrifugation, washed with diethyl ether (20 mL) and dried in vacuo, providing a yellow solid (20 mg, yield 34%). HR-MS (TOF-MS) calculated for $\text{C}_{28}\text{H}_{22}\text{F}_6\text{N}_{10}\text{PdSb}^+ [\text{M}-(\text{SbF}_6)]^+$: $m/z = 841.0011$; observed: $m/z = 841.0090$.

3.4. Experimental Data for the Complex $[\text{Ag}_2\text{L}_2](\text{SbF}_6)_2$

After dissolving the residue from the initial reaction mixture in acetonitrile and fractional crystallization, first by the diffusion of diethyl ether into acetonitrile (giving microcrystals collected by filtration as described above) and then by the slow evaporation of the filtrate, light yellow crystals of the $[\text{Ag}_2\text{L}_2](\text{SbF}_6)_2$ complex were obtained with a 5% yield of the reaction. Elem. Anal. calculated for $\text{C}_{28}\text{H}_{22}\text{F}_{12}\text{N}_{10}\text{Ag}_2\text{Sb}_2 \cdot 7\text{H}_2\text{O}$: C, 25.64; H, 2.77; N, 10.68. Found: C, 25.67; H, 1.65; N, 10.60 (%). No satisfactory elemental analysis was obtained due to its hygroscopic property.

4. Conclusions

In this report, we have described the synthesis and structural analysis of a new binuclear macrocycle in which labile Ag(I) ions are coordinated using a very unique chelating system based on functionalized pyrimidine, bipyridine, and fluorine atoms derived from SbF_6^- counter ions. Moreover, the generated macrocyclic systems undergo further interaction in the solid state, creating a one-dimensional supramolecular polymer in which individual units are connected with each other by hydrogen bonding interactions. Comparison of the now known structures of the Fe(II) and Ag(I) complexes of 5-([2,2'-bipyridin]-5-yl)pyrimidin-2-amine showed that the coordination mode of this ligand is not predictable and clearly can vary considerably with the metal ion chosen. Nonetheless, in both of these known cases the bound ligand retained the capacity to act as an H-bond donor-acceptor, indicating that the solid state supramolecular chemistry has significant prospects for further development, especially with regard to catalytic applications such as those envisaged for the Pd(II) complexes initially targeted in the present work [52,53].

Supplementary Materials: The following are available online, Figure S1: ^1H NMR spectrum (600 MHz) of the reaction mixture $[\text{Pd}^{\text{II}}\text{L}_2](\text{SbF}_6)_2$. Figure S2: ^1H NMR spectrum (600 MHz) of comparisons free ligand and isolated material (see Figure S1) in deuterated MeCN and DMSO. Figure S3: HR-TOF-ESI-MS analysis of the reaction mixture $[\text{Pd}^{\text{II}}\text{L}_2](\text{SbF}_6)_2$. Figure S4: HR-TOF-ESI-MS analysis of the reaction mixture $[\text{Pd}^{\text{II}}\text{L}_2](\text{SbF}_6)_2$. Figure S5: Kinetic ^1H NMR spectrum (600 MHz, CD_3CN) of the reaction mixture $[\text{Pd}^{\text{II}}\text{L}_2](\text{SbF}_6)_2$. Figure S6: Void analysis of complex $[\text{Ag}_2\text{L}_2](\text{SbF}_6)_2$, and complex $[\text{Fe}^{\text{II}}\text{L}_3](\text{BF}_4)_2 \cdot 9\text{H}_2\text{O}$ performed with mercury.

Author Contributions: A.B.-C., A.W., J.M.H., and A.R.S. conceived and designed the experiments; A.W., A.B.-C., and M.G. performed the synthetic work and analyzed the data; J.M.H. and A.R.S. made crucial revisions of the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The crystal data for $[\text{Ag}_2\text{L}_2](\text{SbF}_6)_2$ have been deposited in the Cambridge Crystallographic Data Centre (CCDC) with deposition number CCDC 2065082. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK.

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Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analysis, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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