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Journal Name

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ARTICLE TYPE

Synthesis and Structural Characterization of the Silver(I), Copper(I) Coordination Polymers and the Helicate Palladium(II) Complex of the Dipyrrolylmethane-based Dipyrazole Ligands: The Effect of Meso Substituents on the Structure Formation[†]

[5] **Tapas Guchhait, Bhagyasree Barua, Aritra Biswas, Biswanath Basak and Ganesan Mani*[a]**

A new class of multidentate dipyrrolylmethane based ditopic tecton, 1,9-bis(3,5-dimethylpyrazolylmethyl)dipyrrolylmethane, containing diethyl (L_1) or cyclohexylidene (L_2)
[10] substitutents at the *meso* carbon atom were readily synthesized in 28−45% yields in two different ways starting from dipyrrolylmethanes. One dimensional coordination polymer structure ($[(L_2)Ag][BF_4])_n$ was obtained when L_2 was treated with $AgBF_4$, whereas the analogous reaction between L_1 and $AgBF_4$ afforded the dicationic binuclear metalacycle complex $[(L_1)_2Ag_2][BF_4]_2$. In addition, yet another coordination polymeric structure $[(L_1)CuI]_n$ was obtained from the reaction between L_1 and CuI. The
[15] analogous reaction of L_1 with $[Pd(PhCN)_2Cl_2]$ afforded the binuclear palladium complex $[(L_1)_2Pd_2Cl_4]$ having a double-stranded helicate structure. The observed structural differences are attributed to the effect of substituents present at the *meso* carbon atom of ligand, in addition to the nature of metal centre, coordination number and the preferred geometry.

Although a wide variety of coordination polymers with attractive
[20] supramolecular architectures containing silver(I) atom as node have been reported with a variety of ligand systems[1] mainly N-donors, it continues to be an active area of research because of their potential applications in several areas such as catalysis,[2] gas adsorption,[3] photoluminescence,[4] antibacterial activity,[5] and thin
[25] film precursor.[6] The architecture of the coordination polymer remains very sensitive to the orientation of the ligating atoms in the organic molecule,[7] counter ion,[8] metal-to-ligand ratio,[9] and solvents.[10,11] This is coupled with the flexibility of silver metal to adopt different coordination numbers and geometries with
[30] noncovalent interactions such as hydrogen bonding and π−π interaction among others.[12]

Coordination polymers with silver metal ion are currently being investigated using pyrazole ring incorporated fascinating class of ligand systems such as poly(pyrazolyl)borate and
[35] poly(pyrazolyl)alkane.[13] A subtle change in the framework of poly(pyrazolyl)alkane gives an unique ligand with features of coordinating N-donors and hydrogen bonding groups and a variety of silver(I) coordination polymers have been investigated with different anions, solvents, and metal-to-ligand ratios.[14] For
[40] instance, Reger and co-workers have investigated the influence of rigid and flexible spacer units between two bis(pyrazolyl)methane moieties and counter anions on the formation of cyclic dimer versus linear polymeric chain structure containing silver(I) atom.[15] Similarly, coordination polymers
[45] containing copper(I) atom have been developed with a variety of

ligands[16] some of which possess luminescent property.[17]

Like pyrrole, the pyrrole rings of a dipyrrolylmethane molecule **1** are electron rich and hence readily undergo electrophilic substitution reactions. Sterically demanding
[50] dipyrrolylmethanes can readily be synthesized using suitable starting aldehyde/ketone molecule which puts steric hindrance at the *meso* position. In addition, its α-positions are available for electrophilic substitution.[18] As a result, dipyrrolylmethanes have been used as building block for synthesizing synthetic expanded
[55] porphyrins,[19] calix[*n*]pyrroles[20] and other related compounds.[21] Dipyrrolylmethanes have been used as dianionic multidentate ligands with κ^1/η^5 bonding modes for synthesizing many structurally interesting transition[22] and lanthanide[23] complexes, in which they showed the characteristics of familiar *ansa*
[60] cyclopentadienyl ligand. Further, 1,9-positions functionalized diiminodipyrrolylmethane derivatives and their coordination chemistry have been developed by Love and co-workers[24] and others.[25]

We are interested in synthesizing suitable pyrrole-based
[65] multidentate linear and cyclic molecules by making use of synthetic protocols and the reactive α-positions of pyrrole and dipyrrolylmethane for transition metal complexes. We recently reported a few pyrrole-based multidentate ligand systems: pyrrole-diphosphine, dipyrrolylmethane-diphosphine,[26]
[70] bis(pyrazolylmethyl)pyrrole,[27] tetra(pyrazolylmethyl)pyrrole[28] and their transition metal complexes. Given the variety of pyrrole-based ligands and their rich coordination chemistry

developed, we became interested to investigate the effect of substituents at the *meso* carbon atom of dipyrrolylmethanes on the coordination number, geometry and the supramolecular self assembled structure of metal complexes. Herein, we report

[5] synthesis, structural characterization of two new dipyrrolylmethane derivatives containing 3,5-dimethylpyrazolyl (pz^{Me2}) groups which differ by the *meso* substituents, ethyl or

cyclohexylidene group. In addition, we report the influence of the *meso* substituents on the structure of silver(I), copper(I) and

[10] palladium(II) complexes.

Results and Discussion
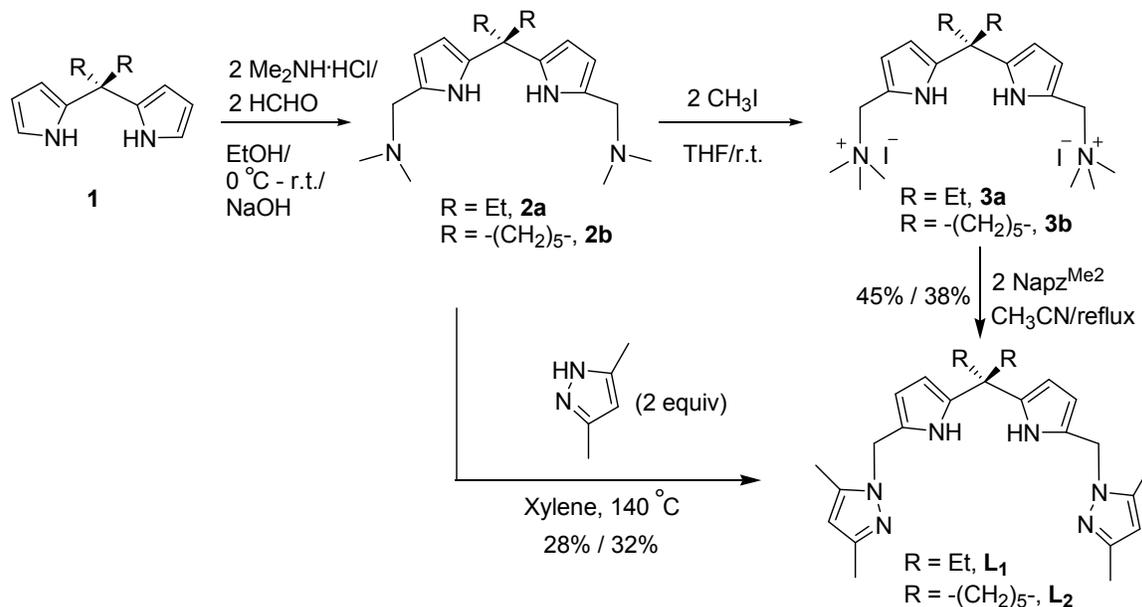
Scheme 1. Synthesis of 1,9-bis(3,5-dimethylpyrazolylmethyl)dipyrrolylmethanes **L₁** and **L₂** by two methods.

[15] ## Synthesis and Characterization of L₁ and L₂

We set the synthesis of the dipyrrolylmethane-based ligands **L₁** and **L₂** containing two pyrazole rings one on each side because they can be a fairly lengthy acyclic ditopic tecton with the features of hydrogen bonding pyrrolic NH groups for anion

[20] binding and the pyrazole nitrogens for cation coordination. In addition, tectons of this type will be suitable for forming large size metallacycles as well as 1D coordination polymers. They can be synthesized by two convenient synthetic methods: one is the direct reaction of the double Mannich base of dipyrrolylmethane

[25] with the neutral pyrazole, which is similar to the synthesis of 2,5-bis(3,5-dimethylpyrazolylmethyl)pyrrole,[27] and the other method involves the treatment of the quarternary ammonium salt of the double Mannich base with pyrazolate anion. It can be noted from Scheme 1, the desired 1,9-

[30] bis(pyrazolylmethyl)dipyrrolylmethanes **L₁** and **L₂** were obtained by both the methods with almost the same yield. **L₁** and **L₂** are probably formed via the nucleophilic attack of 3,5-dimethylpyrazolide on the electrophilic methylene carbon. These two products differ by the *meso* carbon substituents. It is

[35] interesting to note that the steric crowding around the *meso* carbon has a profound effect on the structure of metal complexes as reported by Gambarotta and co-workers.[23] Further, the C_{meso}–$C_{pyrrole}$ $_{\alpha-C}$ rotation gives its flexibility and hence dipyrrolylmethane-based ligands are able to form novel double

[40] helical structures with metal ions.[24b,c,29]

The compounds **L₁** and **L₂** are air stable colorless solid and soluble in common organic solvents. The ^{1}H NMR spectra of **L₁** and **L₂** in CDCl₃ feature broad singlets at δ = 8.45 ppm and 8.97 ppm, respectively, for the pyrrolic NH protons, which are shifted

Fig.1 (a) ORTEP diagram of **L₁** (30% thermal ellipsoids). (b) Its packing diagram shows the intermolecular hydrogen bonding involving the pyrrolic NH and the adjacent pyrazole ring nitrogen atom. Selected bond lengths (Å) and angles (°): N3···N1^i 3.043(4), H1n3···N1^i, 2.20(4), N3–H1n3···N1^i 167(3);

N4···N6^{ii} 3.068(4), H1n4···N6^{ii}, 2.20(3), N4–H1n4···N6^{ii} 176(3). Symmetry transformations used to generate equivalent atoms: (i) −x + 1, −y, −z + 1 (ii) −x + 2, −y, −z + 1.
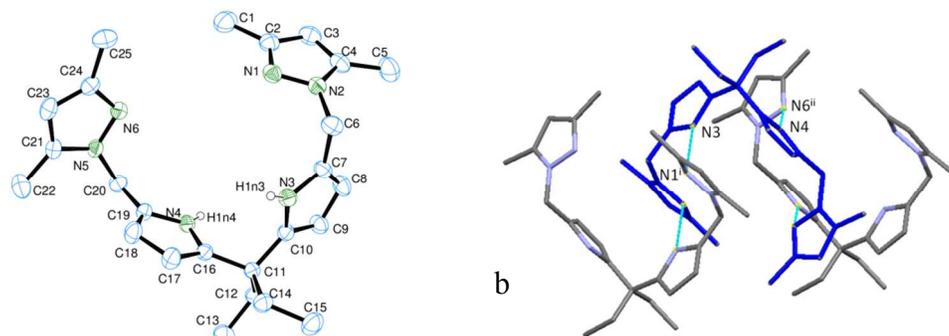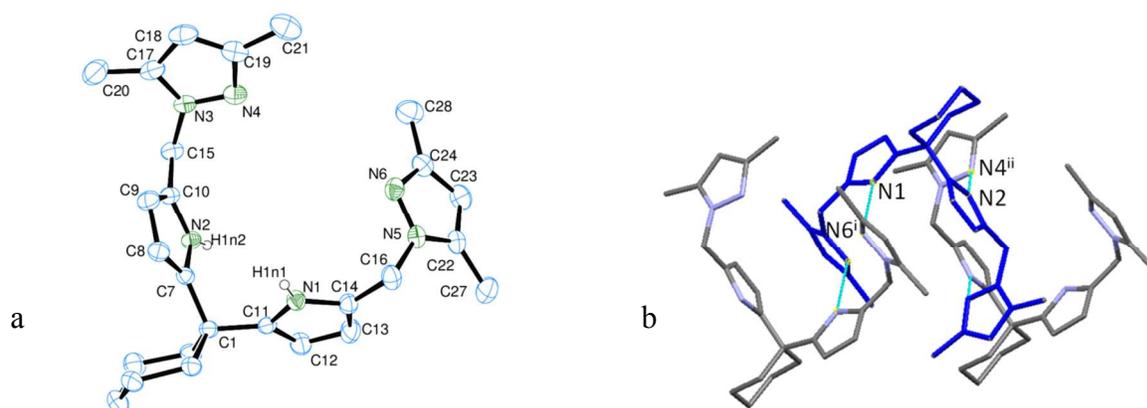

5 **Fig. 2** (a) ORTEP diagram of **L$_2$** (30% thermal ellipsoids). (b) Its packing diagram shows the intermolecular hydrogen bonding involving the pyrrolic NH and the adjacent pyrazole ring nitrogen atom. Selected bond lengths (Å) and angles (°): N1···N6^i 3.055(3), H1n1···N6^i, 2.22(3), N1–H1n1···N6^i 168(2); N2···N4^{ii} 3.017(3), H1n2···N4^{ii} 2.11(3), N2–H1n2···N4^{ii} 173(2). Symmetry transformations used to generate equivalent atoms: (i) −x + 2, −y + 2, −z + 2 (ii) −x + 1, −y + 2, −z + 2.

downfield as compared to the pyrrolic NH resonances for the parent dipyrrolylmethanes **1** or their Mannich bases **2a,b**. The X-ray structures of **L$_1$** and **L$_2$** are given in Fig. 1 and Fig. 2 along with selected bond lengths and angles. In both the structures, the pyrrolic NH groups are oriented in opposite directions so that they can form the intermolecular hydrogen bonding to the pyrazolyl nitrogen atoms of the adjacent molecules in the solid state (Fig. 1b and Fig. 2b). This demonstrates the flexibility of the dipyrrolylmethane moiety resulting from the C$_{meso}$–C$_{pyrrole~\alpha\text{-}C}$ rotation. In addition to this rotation, there can be other rotations involving the methylene carbons (C–C and C–N). As a result, the diastereotopic methylene protons appear as a sharp singlet in the ^{1}H NMR spectra of both the molecules in CDCl$_3$. Their ^{13}C NMR spectra show 13 (**L$_1$**) and 14 (**L$_2$**) peaks, indicating a symmetrical structure in consistent with the X-ray structure.
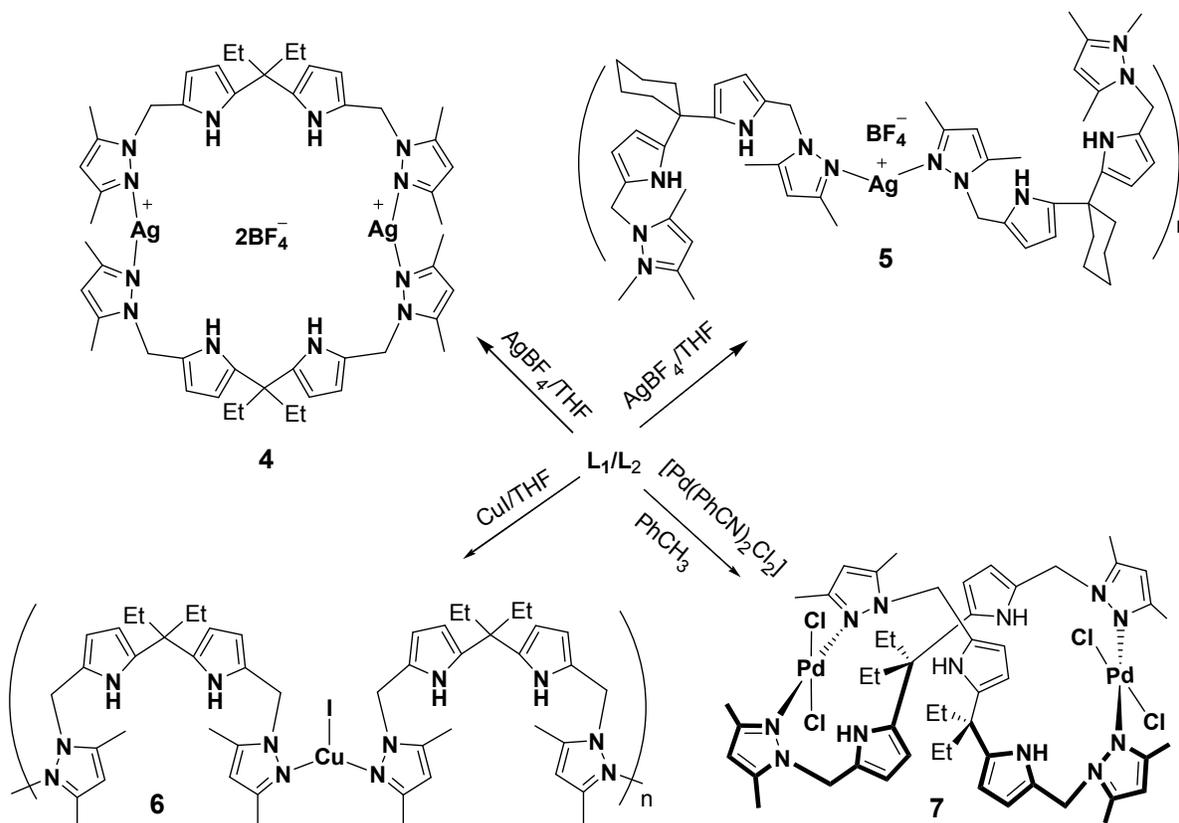
25 **Scheme 2.** Synthesis of the silver(I), copper(I) and palladium(II) complexes featuring the dicationic cyclic, linear coordination polymer and helical structures bearing **L$_1$** and **L$_2$** ligands.

ARTICLE TYPE

Synthesis and Characterization of Metal Complexes of L₁ and L₂

As shown in Scheme 2, ligands **L₁** and **L₂** react with AgBF₄ to give two different complexes: the dicationic metalacycle **4** and

5 the linear coordination polymeric complex **5**. Because the anion is the same for both complexes, the striking structural difference is attributed to the effect of steric crowding imparted by the substitutents at the *meso* carbon atom. One cyclohexylidene group can be more bulkier than two ethyl groups and therefore

10 the cyclic dicationic structure would be unfavourable for ligand **L₂** rather it gives the linear polymeric complex in which the cyclohexylidene groups are oriented opposite to each other. Conversely, the analogous reaction of **L₁** with CuI yielded yet another linear coordination polymeric copper(I) complex **6**. This

15 indicates that the metal centre also plays a crucial role in the structure formation. We also carried out the reaction between **L₁** and [Pd(PhCN)₂Cl₂] to give the binuclear dipalladium complex **7** which is structurally quite different from the silver analogue **4** (see below). All these complexes are characterized by ^{1}H, FTIR,

20 ^{13}C and elemental analysis and their structures were determined by single crystal X-ray diffraction studies. The ^{1}H NMR spectra of metal complexes bearing **L₁** in CD₃CN or CDCl₃ feature deshielded resonances for the methylene and the pyrrolic NH protons relative to the free ligand resonance. In contrast to this,

25 the complex **5** bearing **L₂** shows a slightly shielded resonance for NH proton. The symmetrical structure of complex **4** or **6** is supported by their ^{13}C NMR spectra which show 13 peaks like that of ligand **L₁**. The noticeable difference between the ^{1}H NMR spectra of the cyclic dimer **4** and the polymeric **5** complexes lies

30 in the number of the pyrrole β-CH resonance. While the dimer **4** gives a broad single peak, the polymeric complex **5** gives two broad peaks for their pyrrole β-CH protons in CD₃CN. Conversely, the copper polymeric complex **6** in CDCl₃ gives single broad multiplet for its pyrrole β-CH protons in the ^{1}H

35 NMR spectrum.

In addition, the corresponding reaction of **L₂** with either CuI or palladium has failed to give single crystals suitable for X-ray diffraction. However, the ^{1}H NMR spectrum (see ESI, Fig. S20 & S21) of the copper complex in CDCl₃ or CD₃CN obtained from

40 the reaction of **L₂** with CuI appears to be fairly clean and its pyrrole β-CH resonance pattern resembles that of complex **6**, which is a single broad multiplet in CDCl₃ (see ESI, Fig. S14).
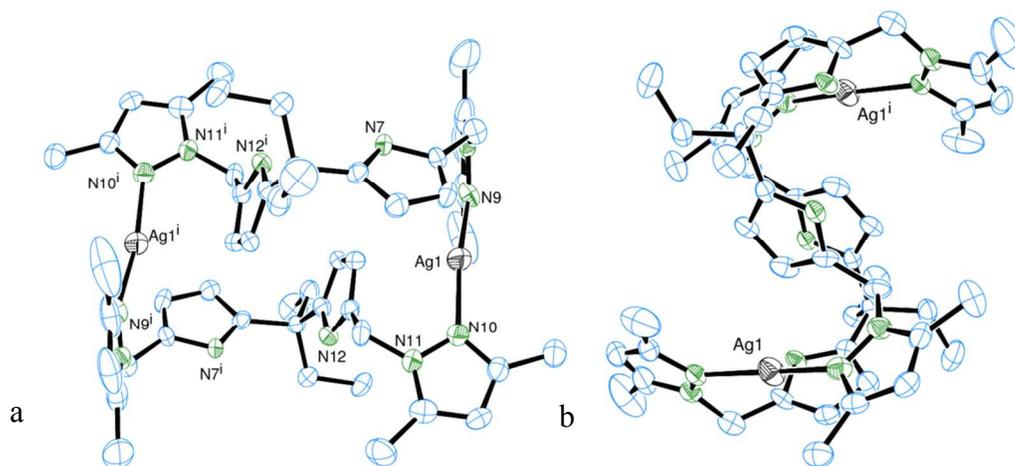

Fig. 3 ORTEP diagram of the dicationic metalacycle silver(I) complex **4** (30% thermal ellipsoids). All hydrogen atoms, BF₄⁻ anions, dichloromethane
45 solvent of crystallization are omitted for clarity. Selected bond lengths (Å) and angles (°): N9–Ag1 2.122(8), N10–Ag1 2.102(8), N10–Ag1–N9 166.8(3), N3–Ag2 2.126(7), N4–Ag2 2.121(7), N4–Ag2–N3 168.6(3). Symmetry transformations used to generate equivalent atoms: (i) −x, −y + 1, −z + 1 and (ii) −x−1, −y, −z.

Complex **4** crystallizes in the triclinic *P*-1 space group. The asymmetric unit consists of two half molecules and two BF₄⁻ ions

50 along with one dichloromethane as solvent of crystallization. The dicationic metalacyclic molecule **4** containing two silver atoms is generated by grow fragment and one of the two molecules is shown in Fig. 3. A side view of the molecule exhibits an 'S' shape conformation in which the two middle pyrrole rings are

55 facing each other (Fig. 3b). Rather than having a fairly open cyclic framework, the 'S' shape is probably due to the steric stain of the molecule. The average Ag···Ag distance is 8.549(3) Å. Each silver(I) atom is two coordinate and adopts a linear geometry with the average N−Ag−N angle value of 167.7(3)°.

60 The Ag−N bond distances vary from 2.102(8) Å to 2.126(7) Å, confirming the two coordinate geometry of the silver atom in the cationic cyclic molecule. These distances are shorter than those observed for complex **5** (see below) and fall within the 1.99(2) Å to 2.149(4) Å range reported for the two coordinate silver(I)

65 complexes bearing pyrazole[30] and multi-pyrazole ligands.[14i, 31]

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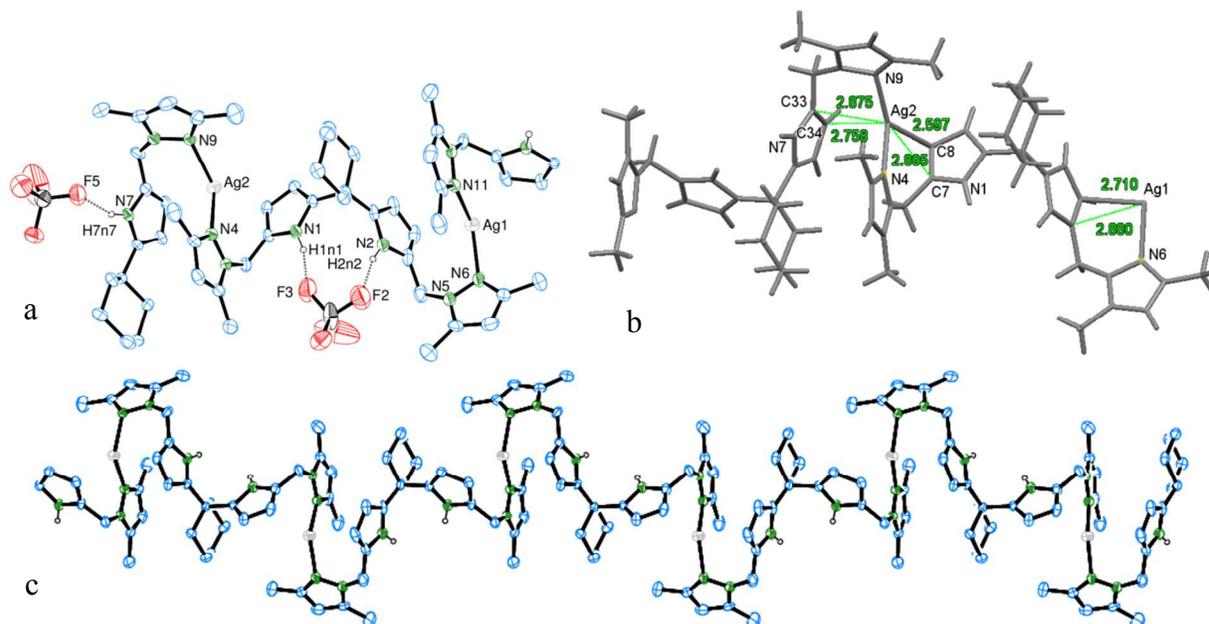Dynamic Article Links ▶

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Fig.4. ORTEP diagram of the silver(I) coordination polymer **5** (30% thermal ellipsoids), most hydrogen and disordered fluorine atoms are omitted for clarity; dotted lines indicate hydrogen bonds: (a) the asymmetric unit, showing the pyrrolic NH hydrogen bonding with BF_4^- anions, (c) showing the short contacts of the pyrrole ring carbons with the silver atom and (c) linear coordination polymer chain. Selected bond lengths (Å) and angles (°): N11–Ag1 2.201(6), N6–Ag1 2.204(7), N9–Ag2 2.202(6), N4–Ag2 2.236(6), N11–Ag1–N6 125.5(2), N9–Ag2–N4 120.4(2), N1···F3 2.809(9), H1n1···F3 1.99(5), N1–H1n1···F3 158(7); N2···F2 2.882(10), H2n2···F2 2.03(4), N2–H2n2···F2 166(7); N7···F5 2.975(8), H7n7···F5 2.16(4), N7–H7n7···F5 159(6). Symmetry transformations used to generate equivalent atoms: (i) x, y, z − 1 and (ii) x, y, z + 1.

Complex **5** crystallizes in the triclinic space group *P*-1 and the asymmetric unit contains two ligands **L₂**, two silver atoms and two disordered BF_4^- ions, thus giving +1 oxidation sate to the silver atom. The two pyrazolyl nitrogen atoms of each ligand coordinate to two different silver atoms, by which, as shown in Fig. 4, the 1D polymeric chain with a zig-zag conformation of the pyrazole rings with the silver-silver distance of 10.259(2) Å is formed. The pyrrolic NH groups are hydrogen bonded to the disordered BF_4^- ions. Although each silver atom is formally two coordinate, each silver(I) atom has two short contacts with the pyrrolic carbon atoms located on both sides (Fig. 4b). These short contact distances range from 2.597(9) Å to 2.895(8) Å which are well below the sum of the van der Walls radii of silver and carbon atoms.[32] If these short contacts are treated as η² or η$^{1.5}$ π-coordination, then the geometry around each silver atom can be tetrahedral and is supported by the average N–Ag–N angle value of 122.9(2)°.

These short contact distances fall in the range 2.4 Å to 2.9 Å reported for several other silver(I) complexes with Ag···C(arene) π-interactions.[33] Besides, these distances are smaller than those found for $[Ag(\kappa^2\text{-}m\text{-}C_6H_4\{C(pz)_2(2\text{-py})\}_2)_2]^+$(pz = pyrazoly, py = pyridyl) (3.193 Å),[34] the trimesityltriazine silver complex (3.102 Å and 3.332 Å),[35] $[Ag\{(pz)_2CPh_2\}_2]^+$ (2.892(2) Å)[36] and others.[37]

Recently, we also reported Ag···C short contacts present in the tetranuclear silver(I) complex of the tetrakis(pyrazolylmethyl)pyrrole ligand (2.894(7) Å and 3.080(6) Å).[28] The silver-pyrazole nitrogen (Ag–N) bond distances range from 2.201 Å to 2.236 Å which are slightly longer than those reported for the two coordinate silver(I) complexes bearing pyrazole (1.99(2) Å to 2.149(4) Å)[30] and multi-pyrazole ligands.[31, 14i] Further, these distances are slightly longer than the range 2.117(5) to 2.205(5) Å reported for the two coordinate tetranuclear silver(I) complex of the tetrakis(pyrazolylmethyl)pyrrole ligand reported by us, but remain shorter than the distances in the three coordinate silver(I) complex containing pyrazole ligand.[38]

The difference in Ag–N bond distances between the structures of complex **4** and **5** can be attributed to the coordination number of the silver atom. Because of the short contacts of silver atom in the structure of **5**, its N–Ag–N angle is relatively more bent and the Ag–N distance is longer than those in the structure of **4** in which each silver atom is two coordinate. This is consistent with the electroneutrality principle which was used to explain the Ag–N bond distances found in the reported silver complex structure.[39]
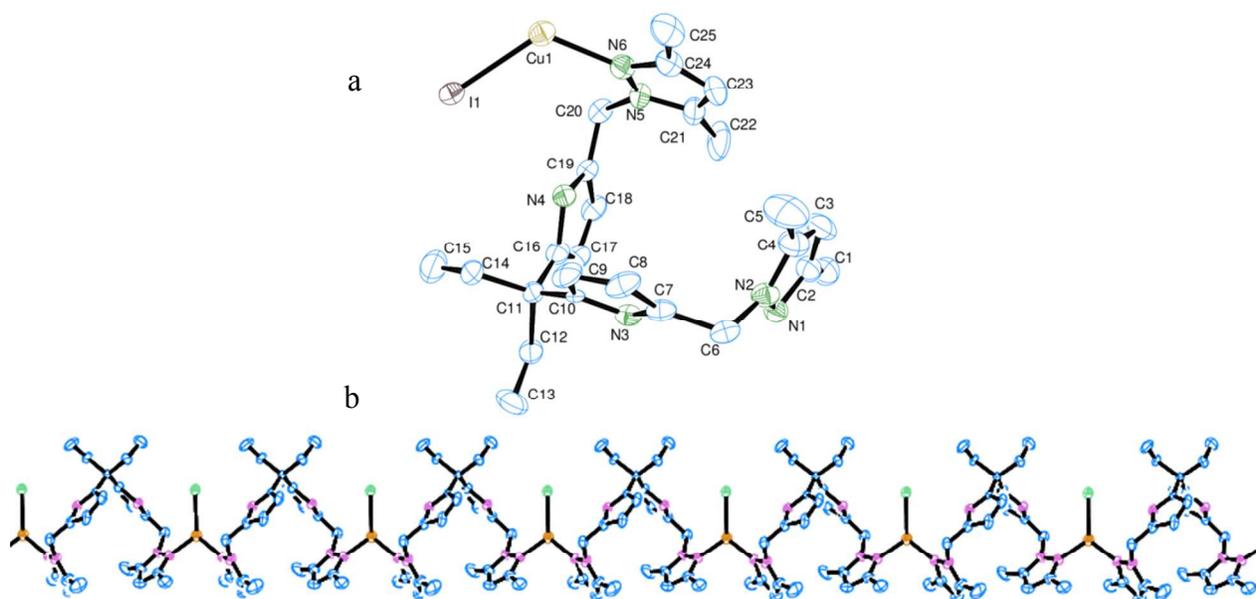
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Fig.5. ORTEP diagram of the copper(I) linear coordination polymer **6** (30% thermal ellipsoids), all hydrogen atoms are omitted for clarity: (a) the asymmetric unit and (b) 1D coordination polymer chain. Selected bond lengths (Å) and angles (°): Cu1–I1 2.4988(15), N6–Cu1 2.015(9), N6–Cu1–I1 123.7(2), N1^{ii}–Cu1–N6 108.5(3), N1^{ii}–Cu1–I1 127.7(2). Symmetry transformations used to generate equivalent atoms: (i) x + 1, y, z, (ii) x − 1, y, z.

Complex **6** crystallizes in the monoclinic space group $P2_1/n$. The asymmetric unit consists of one **L₁** and one Cu–I moiety (Fig. 5a). The copper atom is coordinated by two pyrazole nitrogen atoms from two ligands, thus forming a three coordinate copper(I) complex. The other side pyrazole nitrogen atom of each ligand coordinates in the same way, which grows into a linear 1D polymeric chain with all Cu–I groups oriented in one direction (Fig. 5b). The geometry around each copper atom is trigonal planar with the N−Cu−N angle of 108.5(3)° which is smaller than the other two angles, 123.7(2)° and 127.7(2)° and remains greater than that (104.0°) reported for a similar copper(I) polymer chain formed by a Schiff base ligand.[40] In addition, the two pyrrolic NH groups are oriented in opposite directions and hydrogen bonded to the iodine atom; the *meso* substituents are on the same side, which is in contrast to the silver(I) coordination polymer **5** formed by **L₂**.
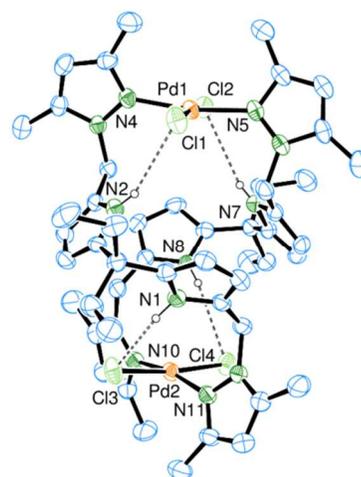
Fig. 6 ORTEP diagram of the binuclear palladium complex **7** (30% thermal ellipsoids), showing a double-stranded helicate view. Most hydrogen atoms and four acetonitrile molecules are omitted for clarity. Dotted lines indicate hydrogen bonds. Selected bond lengths (Å) and angles (°): N4–Pd1 2.013(6), N5–Pd1 2.010(6), N10–Pd2 2.015(6), N11–Pd2 2.001(6), N5–Pd1–N(4) 170.3(2), N5–Pd1–Cl1 90.58(16), N4–Pd1–Cl1 88.85(16), N5–Pd1–Cl2 89.39(16), N4–Pd1–Cl2 92.19(16), Cl1–Pd1–Cl2 173.98(8).

Complex **7** crystallizes in the centrosymmetric triclinic space group *P*-1 and the asymmetric unit contains one molecule of **7** and four acetonitrile as solvent of crystallization. The X-ray structure revealed that the binuclear palladium complex contains

two ligands **L₁**. Each ligand is twisted and the pyrazole nitrogens are bound to the palladium atom, giving a double-stranded helicate structure with Pd···Pd distance of 8.434(2) Å. This is similar to Mn, Fe, Co and Zn helicate structures containing diiminodipyrrolylmethane ligands reported by Love and co-workers.[24b,c,29] The pyrrolic NH groups of each ligand are pointed opposite to each other which is probably because of the twist in the ligand framework and hydrogen bonded to the chlorine atom of the Pd–Cl unit. Each palladium adopts a slightly distorted square planar geometry as shown by their angles which are closer to the ideal values of 90° and 180°. The Pd–N bond distances range from 2.001(6) to 2.015(6) Å and are in the range reported for palladium complexes containing the pyrazole nitrogen coordination.[27] A few interesting differences are noted upon comparison of this dipalladium complex **7** with the binuclear silver complex **4**. The ligand twist and the resulting pyrrolic NH opposite orientations are not observed in the silver complex **4** which are probably because of different coordination number and geometry that these two metals adopt. Further, the ¹H NMR spectrum of **7** in CDCl₃ shows two resonances for the pyrrolic NH protons at δ = 9.57 and 9.49 ppm and the methylene protons display AB patterns with J(HH) = 17 Hz which are overlapped with the resonances due to the pyrrolic β-CH and pyrazole CH protons (See ESI, Fig. S18). On the other hand, the silver complex **4** gives a simple spectrum.

Conclusions

Two new multidentate 3,5-dimethylpyrazole substituted dipyrrolylmethane ligands were synthesized in a convenient way and structurally characterized. It is interesting to note that the coordination polymeric structure was obtained when the ligand contains the cyclohexylidene group (**L₂**) at the *meso* carbon atom of the dipyrrolylmethane ligand, whereas **L₁** with ethyl groups at the *meso* carbon gave complexes having different structures featuring cyclic, coordination polymer and helicate. This difference in the structure formation remains primarily attributable to the steric influence of the *meso* carbon substituents, which possess such a direction power. In addition, the formation of copper coordination polymer and helicate palladium complexes containing the same liand **L₁** suggests the role of metal center in the structure formation. To the best of our knowledge, this is the first report of coordination polymer versus cyclic structure formation using the dipyrrolylmethane based ditopic tecton. Synthesis of other metal complexes and their catalytic applications are under progress.

Experimental section

Solvents were purchased from commercial sources and distilled before use by following standard procedures. Diethyldipyrrolylmethane,[41] 1,1′-dipyrrolylcyclohexane,[23f] 1,9-bis(N,N-dimethylaminomethyl)dipyrrolylmethanes,[42] were prepared according to the literature procedures. Pyrrole, dimethylamine hydrochloride, 3-pentanone, 3,5-dimethylpyrazole were purchased from Aldrich and were used without further purification except pyrrole, which was distilled, and amine hydrochloride, which was dried under vacuum with warm water.

Formaldehyde, methyl iodide and other reagents were purchased from local commercial sources. ¹H NMR (200 MHz or 400 MHz) and ¹³C NMR (50.3 or 100.6 MHz) spectra were recorded on a Bruker ACF200 or AV400 spectrometer. Chemical shifts are referenced with respect to the chemical shift of the residual protons present in the deuterated solvents. FTIR spectra were recorded using Perkin Elmer Spectrum Rx. High Resolution Mass Spectra (ESI) were recorded using the Xevo G2 Tof mass spectrometer (Waters). Elemental analyses were carried out using a Perkin−Elmer 2400 CHN analyzer. Melting points were determined in open capillaries and are corrected using benzophenone as a reference.

Synthesis of 1,9-bis(3,5-dimethylpyrazolylmethyl)-5,5′-diethyldipyrrolylmethane L₁: Method a
(a) Synthesis of 3a
To a solution of 1,9-bis(N,N-dimethylaminomethyl)diethyldipyrrolylmethane **2a** (4.30 g, 12.86 mmol) in THF (150 mL) was added CH₃I (2.00 mL, 32.14 mmol) drop wise at room temperature with stirring. The stirring was continued for 4 h, resulting in the formation of colorless precipitate. The precipitate was filtered, washed with THF several times and dried under vacuum to give **3a** as colorless solid (7.13 g, 11.87 mmol, 92% yield).

(b) Synthesis of L₁
To a solution of NaH (0.57 g, 23.74 mmol) in methanol (20 mL) was added 3,5-dimethylpyrazole (2.28 g, 23.72 mmol), generating an exothermic reaction. The solution was stirred for 15 minutes at room temperature and the solvent was removed under vacuum to give the sodium salt of 3,5-dimethylpyrazole as an oily paste. This residue was taken in acetonitrile (300 mL) and the quaternary ammonium salt **3a** (7.13 g, 11.87 mmol) was added. The resulting solution was refluxed at 100–110 °C for 30 h. The solution was cooled to room temperature and filtered. The solvent was removed under vacuum and the resulting residue was loaded onto a column filled with silica gel. Elution using ethylacetate and petroleum ether mixture (2 : 1 v/v) afforded the first fraction from which the solvent was removed to give **L₁** as colorless solid (2.24 g, 5.35 mmol, 45%). The suitable single crystals for X-ray diffraction study were obtained from 2 : 1 ethylacetate and petroleum ether mixture upon slow evaporation.

Method b To a solution of 1,9-bis(N,N-dimethylaminomethyl)diethyldipyrrolylmethane **2a** (2.00 g, 5.98 mmol) in xylene (60 mL) was added 3,5-dimethylpyrazole (1.30 g, 13.52 mmol). The solution was refluxed at 140 °C for 24 h. The reaction mixture was cooled to room temperature and the solvent was removed under vacuum. The resulting residue was loaded onto a column filled with silica gel. Elution using ethylacetate and petroleum ether mixture (1 : 1 v/v) afforded the first fraction from which the solvent was removed to give **L₁** as colorless solid (0.70 g, 1.67 mmol, 28%). mp 166 °C. ¹H NMR (200 MHz, CDCl₃, 25 °C, ppm): δ = 0.63 (t, 6H, ³J(H,H) = 7.0 Hz, CH₂*Me*), 1.85 (q, 4H, ³J(H,H) = 7.0 Hz, C*H₂*Me), 2.17 (s, 12H, pyrazole *Me*), 4.99 (s, 4H, pyrrole α-C*H₂*), 5.73 (s, 2H, pyrazole C*H*), 5.83 (t, 2H, ³J(H,H) = 2.0 Hz, pyrrole β-C*H*), 5.91 (d, 2H, ³J(H,H) = 2.0 Hz, pyrrole β-C*H*), 8.45 (br s, 2H, N*H*). ¹³C{¹H} NMR (50.3 MHz, CDCl₃, 25 °C, ppm): δ = 8.5, 11.2, 13.5, 29.6, 43.7, 46.0, 105.46, 105.54, 106.2, 125.9, 137.6, 139.1,

147.5. FT-IR (KBr, cm^{-1}): ν = 3220 (vs), 3155 (m), 3113 (m), 2970 (s), 2931 (m), 2874 (m), 1734 (w), 1718 (w), 1700 (w), 1654 (w), 1578 (w), 1547 (s), 1508 (w), 1460 (s), 1432 (m), 1388 (s), 1378 (m), 1345 (m), 1308 (m), 1264 (w), 1205 (m), 1113 (w), 1048 (w), 1029 (m), 994 (w), 926 (w), 779 (vs), 686 (m), 636 (w), 469 (w). HRMS (+ESI): calcd m/z for [M + Na$^+$] C$_{25}$H$_{34}$N$_6$Na: 441.2743, found: 441.2721.

Synthesis of 1,1′-bis[2-(3,5-dimethylpyrazolylmethyl)-5-pyrrolyl]cyclohexane, L$_2$. Method a:

(a) Synthesis of 3b To a solution of 1,1′-bis[2-(N,N-dimethylaminomethyl)-5-pyrrolyl]cyclohexane **2b** (1.60 g, 4.62 mmol) in THF (60 mL) was added CH$_3$I (0.72 mL, 11.54 mmol) drop wise at room temperature with stirring. The stirring was continued for 4 h, resulting in the formation of colorless precipitate. The precipitate was filtered, washed with THF several times and dried under vacuum to give **3b** as pale yellow solid (2.64 g, 4.31 mmol, 93%).

(b) Synthesis of L$_2$ To a solution of NaH (0.12 g, 5.00 mmol) in methanol (15 mL) was added 3,5-dimethylpyrazole (0.47 g, 4.90 mmol), generating an exothermic reaction. The solution was stirred for 15 minutes at room temperature and the solvent was removed under vacuum to give the sodium salt of 3,5-dimethylpyrazole as an oily paste. This residue was taken in acetonitrile (200 mL) and the quaternary ammonium salt **3b** (1.50 g, 2.45 mmol) was added. The resulting solution was refluxed at 100–110 °C for 30 h. The solution was cooled to room temperature and filtered. The solvent was removed under vacuum and the resulting residue was loaded onto a column filled with silica gel. Elution using ethylacetate and petroleum ether mixture (2 : 1 v/v) afforded the first fraction from which the solvent was removed to give **L$_2$** as colorless solid (0.40 g, 0.93 mmol, 38%). The suitable single crystals for X-ray diffraction study were obtained from 2 : 1 ethylacetate and petroleum ether mixture upon slow evaporation.

Method b To a solution of 1,1′-bis[2-(N,N-dimethylaminomethyl)-5-pyrrolyl]cyclohexane **2b** (3.82 g, 11.02 mmol) in xylene (100 mL) was added 3,5-dimethylpyrazole (2.54 g, 26.42 mmol). The solution was refluxed at 140 °C for 24 h. The reaction mixture was cooled to room temperature and then the solvent was removed under vacuum. The resulting residue was loaded onto a column filled with silica gel. Elution using ethylacetate and petroleum ether mixture (1 : 1 v/v) afforded the first fraction from which the solvent was removed to give **L$_2$** as colorless solid (1.5 g, 3.48 mmol, 32%). mp 173 °C. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, ppm): δ = 1.48 (m, 6H, cyclohexylidene CH_2), 2.01 (m, 4H, cyclohexylidene CH_2), 2.19 (s, 6H, pyrazole Me), 2.20 (s, 6H, pyrazolyl Me), 4.98 (s, 4H, pyrrole α-CH_2), 5.73 (s, 2H, pyrazole CH), 5.81 (t, 2H, ^3J(H,H) = 3.0 Hz, pyrrole β-CH), 5.94 (t, 2H, ^3J(H,H) = 3.0 Hz, pyrrole β-CH), 8.97 (br s, 2H, NH). ^{13}C{^{1}H} NMR (50.3 MHz, CDCl$_3$, 25 °C, ppm): δ = 11.1, 13.5, 22.8, 26.1, 36.9, 39.9, 45.9, 104.0, 105.4, 106.4, 125.7, 138.8, 139.1, 147.5. FT-IR (KBr, cm^{-1}): ν = 3218 (vs), 3154 (s), 3109 (m), 2931 (vs), 2855 (m), 1720 (w), 1702 (w), 1687 (w),1656 (w), 1638 (w), 1581 (w), 1548 (s), 1479 (m), 1459 (m), 1445 (m), 1418 (m), 1381 (m), 1346 (m), 1307 (m), 1274 (w), 1202 (w), 1188 (w), 1113 (w), 1043 (w), 1029 (m), 993 (w), 827 (m), 806 (m), 776 (vs), 687 (m), 638 (w).

HRMS (+ESI): calcd m/z for [M + H$^+$] C$_{26}$H$_{35}$N$_6$: 431.2923, found: 431.2901.

Synthesis of [(L$_1$)$_2$Ag$_2$][BF$_4$]$_2$, 4

To a THF (50 mL) solution of **L$_1$** (0.10 g, 0.24 mmol) was added solid AgBF$_4$ (0.051 g, 0.26 mmol) under nitrogen atmospheric in dark. After stirring the solution for 1 day at room temperature, the solvent was removed fully and the resulting residue was washed with petroleum ether (50 mL) 2 or 3 times. The residue was extracted with dichloromethane and the solution was filtered. The filtrate was layered with petroleum ether to give colorless crystals of **4** formed over a period of two days. The crystals were separated and dried under vacuum (0.115 g, 0.088 mmol, 73%). mp >155 °C. ^{1}H NMR (400 MHz, CD$_3$CN, 25 °C, ppm): δ = 0.76 (t, 12H, ^3J(H,H) = 3.7 Hz, CH$_2$$Me$), 2.24 (s, 12H, pyrazole Me), 2.35 (s, 12H, pyrazole Me), 5.07 (s, 8H, pyrrole α-CH_2), 5.45 (s, 2H, CH$_2$Cl$_2$), 5.94 (s, 4H, pyrazole CH), 6.05 (s, 8H, pyrrole β-CH), 8.53 (br s, 4H, NH). ^{13}C{^{1}H} NMR (50.3 MHz, CD$_3$CN, 25 °C, ppm): δ = 8.8, 11.8, 15.2, 28.0, 45.1, 46.4, 106.9, 107.0, 108.2, 125.4, 138.9, 143.9, 150.6. FT-IR (KBr, cm^{-1}): ν = 3384 (m), 3128 (w), 2967 (m), 2935 (w), 2880 (w), 1578 (w), 1551 (m), 1464 (m), 1424 (m), 1388 (m), 1266 (m), 1199 (w), 1108 (s), 1052 (vs), 787 (s), 737 (w), 686 (w), 521 (w). Anal. Calcd for C$_{50}$H$_{68}$Ag$_2$B$_2$F$_8$N$_{12}$(without dichloromethane solvent of crystallization): C, 48.96; H, 5.59; N, 13.70. Found: C, 48.84; H, 5.53; N, 13.66.

Synthesis of ([(L$_2$)Ag][BF$_4$])$_n$, 5

To a THF (50 mL) solution of **L$_2$** (0.10 g, 0.23 mmol) was added solid AgBF$_4$ (0.045 g, 0.23 mmol) under nitrogen atmospheric in dark. After stirring the solution for 1 day at room temperature, the solvent was removed fully and the resulting residue was washed with petroleum ether (50 mL) 2 or 3 times. The residue was extracted with acetonitrile and the solution was filtered. The filtrate was layered with diethyl ether to give colorless crystals of **5** formed over a period of one week. The crystals were separated and dried under vacuum (0.036 g, 0.06 mmol, 26%) mp: decomposes above 120 °C. ^{1}H NMR (400 MHz, CD$_3$CN, 25 °C, ppm): δ = 1.47 (m, cyclohexylidene CH_2), 1.51 (m, cyclohexylidene CH_2), 2.23(m, cyclohexylidene CH_2), 2.18 (s, 6H, pyrazole Me), 2.26 (s, 6H, pyrazolyl Me), 5.02 (s, 4H, pyrrole α-CH_2), 5.83 (t, 2H, ^3J(H,H) = 2.0 Hz, pyrrole β-CH), 5.92 (s, 2H, pyrazole CH), 6.01 (t, 2H, ^3J(H,H) = 2.0 Hz, pyrrole β-CH), 8.63 (br s, 2H, NH). ^{13}C{^{1}H} NMR (50.3 MHz, CD$_3$CN, 25 °C, ppm): δ = 10.5, 13.6, 22.6, 25.6, 34.9, 40.3, 45.3, 77.3, 77.9, 78.6, 104.0, 105.5, 107.5, 124.5, 139.1. FT-IR (KBr, cm^{-1}): ν = 3355 (s), 2944 (m), 2857 (w), 1578 (w), 1551 (m), 1459 (m), 1424 (m), 1388 (w), 1283 (w), 1262 (m), 1115 (vs), 1065 (vs), 1033 (vs), 1000 (s), 975 (m), 791 (s), 770 (vs), 680 (w), 519 (w). Anal. Calcd for C$_{26}$H$_{34}$AgBF$_4$N$_6$: C, 49.94; H, 5.48; N, 13.44. Found: C, 49.87; H, 5.66; N, 13.49.

Synthesis of [(L$_1$)CuI]$_n$, 6

To a suspension of CuI (0.1 g, 0.52 mmol) in THF (75 mL) was added **L$_1$** (0.22 g, 0.51 mmol). The resulting suspension was stirred at room temperature for 1 day giving almost clear colorless solution. The solution was filtered and layered with petroleum ether. The colorless crystals of complex **6** were formed over a period of two weeks. The crystals were separated and dried

under vacuum (0.29 g, 0.48 mmol, 92%). mp 168 °C. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, ppm): δ = 0.69 (t, 6H, ^3J(H,H) = 7.0 Hz, CH$_2$*Me*), 1.92 (q, 4H, ^3J(H,H) = 7.0 Hz, C*H$_2$*Me), 2.25 (s, 6H, pyrazole *Me*), 2.30 (s, 6H, pyrazole *Me*), 5.27 (s, 4H, pyrrole α-C*H$_2$*), 5.83 (s, 2H, pyrazole C*H*), 5.93 (t, 4H, ^3J(H,H) = 3.0 Hz, pyrrole β-C*H*), 8.73 (br s, 2H, N*H*). ^{13}C{^{1}H} NMR (50.3 MHz, CDCl$_3$, 25 °C, ppm): δ = 8.6, 11.6, 14.3, 29.6, 43.8, 45.8, 106.1, 106.6, 107.0, 124.7, 137.6, 140.3, 148.4. FT-IR (KBr, cm^{-1}): ν = 3370 (vs), 2964 (m), 2930 (m), 2874 (w), 1552 (s), 1493 (w), 1465 (m), 1423 (s), 1377 (m), 1344 (m), 1302 (w), 1264 (w), 1196 (m), 1041 (m), 926 (w), 768 (vs), 750 (m), 685 (w), 633 (w), 516 (w). Anal. Calcd for C$_{25}$H$_{34}$CuIN$_6$: C, 49.30; H, 5.63; N, 13.80. Found: C, 49.28; H, 5.68; N, 13.81. HRMS (+ESI): calcd *m/z* for [M − I]$^-$ C$_{25}$H$_{34}$N$_6$Cu: 481.2241, found: 481.2170.

Synthesis of [(L$_1$)$_2$Pd$_2$Cl$_4$], 7

To a solution of **L$_1$** (0.055 g, 0.13 mmol) in toluene (50 mL) was added solid [Pd(PhCN)$_2$Cl$_2$] (0.050 g, 0.13 mmol) with stirring. After stirring the solution for 1 day at room temperature, the solution became pale yellow and the solvent was removed under vacuum. The resulting residue was washed with petroleum ether 2 or 3 times and dissolved in minimum amount of dichloromethane (~5 mL) which was mixed with petroleum ether (150 mL) in a beaker, giving a yellow precipitation. The solution was filtered and the precipitate was dried under vacuum to give complex **7** as yellow solid (0.06 g, 0.05 mmol, 77% (without acetonitrile). Suitable single crystals were obtained from CH$_3$CN/MeOH (v/v 10:1) mixture upon slow evaporation. mp >200 °C. ^{1}H NMR (200 MHz, CDCl$_3$, 25 °C, ppm): δ = 0.44 (t, 6H, ^3J(H,H) = 8.0 Hz, CH$_2$*Me*), 0.63 (t, 6H, ^3J(H,H) = 8.0 Hz, CH$_2$*Me*), 1.86 (m, 8H, C*H$_2$*Me), 2.01 (s, 3H, *CH$_3$*CN), 2.20 (s, 6H, pyrazolyl-*Me*), 2.22 (s, 6H, pyrazolyl-*Me*), 2.76 (s, 6H, pyrazolyl-*Me*), 2.93 (s, 6H, pyrazolyl-*Me*), 5.13-6.42 (m, 20H, pyrrole *β*-C*H,* C*H$_2$,* and pyrazole CH), 9.49 (br s, 2H, N*H*), 9.57 (br s, 2H, N*H*). FT-IR (KBr, cm^{-1}): ν = 3325 (vs), 2966 (s), 2927 (m), 2873 (w), 1656 (w), 1560 (s), 1495 (m), 1470 (m), 1422 (vs), 1387 (m), 1338 (m), 1309 (m), 1207 (m), 1040 (m), 992 (w), 927 (w), 884 (w), 778 (vs), 750 (m), 688 (w). Anal. Calcd for C$_{50}$H$_{68}$Cl$_4$N$_{12}$Pd$_2$: C, 50.39; H, 5.75; N, 14.10. Found: C, 49.74; H, 5.76; N, 14.00. HRMS (+ESI): calcd *m/z* for [**7**−**L$_1$**−4Cl−Pd]$^+$ C$_{25}$H$_{34}$N$_6$Pd: 524.1880, found: 524.1811.

Table 1. Crystallographic data for **L$_1$**, **L$_2$**, [(**L$_1$**)$_2$Ag$_2$][BF$_4$]$_2$ (**4**), ([(**L$_2$**)Ag][BF$_4$])$_n$ (**5**), [(**L$_1$**)CuI]$_n$ (**6**) and [(**L$_1$**)$_2$Pd$_2$Cl$_4$] (**7**).

	L$_1$	L$_2$	4	5	6	7
Empirical formula	C$_{25}$H$_{34}$N$_6$	C$_{26}$H$_{34}$N$_6$	C$_{51}$H$_{70}$Ag$_2$B$_2$Cl$_2$F$_8$N$_{12}$	C$_{52}$H$_{68}$Ag$_2$B$_2$F$_8$N$_{12}$	C$_{25}$H$_{34}$CuIN$_6$	C$_{58}$H$_{80}$Cl$_4$N$_{16}$Pd$_2$
Formula weight	418.58	430.59	1311.45	1250.54	609.02	1355.98
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	P$\bar{1}$	P$\bar{1}$	P$\bar{1}$	P$\bar{1}$	P2(1)/n	P$\bar{1}$
a/Å	9.324(5)	9.480(3)	13.881(5)	12.5254(18)	9.8269(14)	12.737(3)
b/Å	11.439(5)	11.937(3)	14.747(5)	12.5882(18)	21.536(3)	15.497(3)
c/Å	12.290(5)	12.185(4)	14.992(5)	19.034(3)	13.757(2)	17.031(4)
$α$/degree	67.236(5)	93.786(9)	94.048(5)	86.019(5)	90.00	85.626(6)
$β$/degree	77.689(4)	107.308(9)	95.837(5)	89.755(5)	106.645(4)	76.215(7)
$γ$/degree	80.129(5)	111.810(8)	105.845(5)	65.575(4)	90.00	81.105(6)
Volume (Å^3)	1175.2(9)	1197.8(6)	2921.4(17)	2725.0(7)	2789.4(7)	3222.8(12)
Z	2	2	2	2	4	2
D_{calcd}, g cm^{-3}	1.183	1.194	1.491	1.524	1.450	1.397
$μ$/mm^{-1}	0.073	0.073	0.833	0.794	1.912	0.773
$F(000)$	452	464	1340	1280	1232	1400
$θ$ range (degree)	1.82 to 25.00	1.79 to 24.99	1.37 to 25.00	1.07 to 25.00	1.81 to 24.88	1.66 to 25.00
Total/ unique no. of reflns.	13815/ 4094	14279 / 4210	35491 / 10268	32876 / 9541	32010 / 4840	37633 / 11293
R_{int}	0.1198	0.0439	0.1623	0.0847	0.1166	0.0738
Data / restr./ params.	4094 / 0 / 286	4210/ 0 / 295	10268 / 79 / 717	9541 / 33 / 707	4840 / 0 / 298	11293 / 0 / 737
GOF (F^2)	0.981	1.024	0.958	1.032	1.109	1.031
$R1$, $wR2$	0.065, 0.1367	0.0535, 0.1294	0.0709, 0.1354	0.0659, 0.1570	0.0731, 0.1563	0.0670, 0.1856
$R1$, $wR2$(all data)	0.1733, 0.1785	0.1010, 0.1519	0.2173, 0.1894	0.1370, 0.1967	0.1473, 0.1877	0.0980, 0.2100
Largest different peak and hole (e Å^{-3})	0.216 and −0.197	0.217 and −0.204	0.694 and −0.618	0.915 and −0.759	3.580 and −0.624	2.422 and −0.747

X-ray Crystallography Suitable single crystals of **L$_1$**, **L$_2$**, **4-7** were obtained from solvents mentioned in their respective synthetic procedures. Single crystal X-ray diffraction data collections for these crystals were performed using a Bruker-APEX-II CCD diffractometer with graphite monochromated molybdenum K$_α$ radiation (λ = 0.71073 Å). The structures were solved by SIR-92[43] available in the WinGX program which successfully located most of the non-hydrogen atoms. Subsequently, least square refinements were carried out on F^2 using SHELXL-97[44] (WinGX version) to locate the remaining non-hydrogen atoms. Typically for all the structures, hydrogen atoms attached to carbon atoms were fixed in calculated positions. In most cases, the pyrrolic NH hydrogen atoms were located from the difference Fourier map and freely refined

isotropically with their thermal parameters set as equivalent to 1.2 times that of their parent atoms. In both silver(I) complexes **4** and **5**, the BF_4^- anions are severely disordered and were handled successfully using EADP and SADI. In case of complex **6**, the pyrrolic NH hydrogen atoms were fixed. The refinement data for all the structures are summarized in Table 1. The residual electron density for the structures **6** and **7** are 3.580 e Å^{-3} and 2.422 e Å^{-3}, respectively, which could not be modelled to an atom or group that will be supported by their spectroscopic data. Further, repeated data collections were also not helpful and gave similar largest different peak values.

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Notes and references

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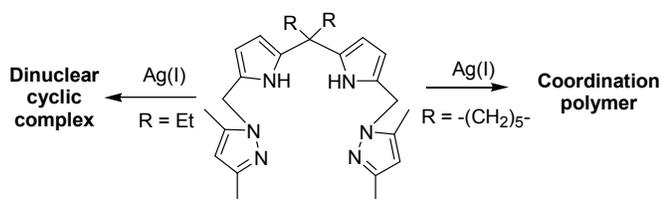
The striking difference in the structures of silver complexes was observed because of the different substituents at the *meso* carbon atom of the dipyrrolylmethane-based ligand. Yet another coordination polymer containing copper(I) and a double-stranded helicate dipalladium complexes are structurally characterized.