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Supramolecular Architecture of a Silver(I) Coordination Polymer Supported by a New Ligand Containing Four Tris(pyrazolyl)methane Units

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The synthesis of coordination polymers is currently of great interest as a method for the construction of new supramolecular architectures. We are developing new 1D, 2D, and 3D coordination polymers based on linking together two or more tris(pyrazolyl)methane units in one ligand. This chemistry builds on our recently reported substantial improvements in the preparations of these ligands and the development of chemistry with them where the central methine carbon atom can be functionalized with groups other than hydrogen.[1] Reported here are the synthesis and preparation of the silver(I) coordination polymer of a new ligand that links four tris(pyrazolyl)methane groups in one molecule, 1,2,4,5-$C_6H_2[CH_2OCH_2C(pz)_3]_4$ (**1**, pz = pyrazolyl ring). This ligand combines the important design characteristics of the rigid architecture of facial bonding encoded in each of the four tris(pyrazolyl)methane groups with flexible sidearms on the arene ring that allow different orientations of the binding groups.

Ligand **1** was prepared[2] according to Scheme 1, and its structure was determined by X-ray crystallography.[3] The solid-state structure, Figure 1, consists of discrete molecules without significant intermolecular associations. Within each tris(pyrazolyl)methane unit the orientation of the three pyrazolyl rings is a propeller arrangement. The adjacent arms of the ligand are oriented above and below the arene ring plane, with one arm twisted away from the other. This orientation is sustained by an intramolecular $C-H\cdots\pi$ interaction between a methylene hydrogen next to the arene ring on the arm that is twisted away and a pyrazolyl ring on the adjacent arm. The hydrogen atom is oriented over the pyrazolyl ring at a distance of 2.941 Å and the corresponding carbon atom at a distance of 3.670 Å. These values are typical for $C-H\cdots\pi$ interactions.[4] The molecule is centrosymmetric, orienting the 1,4 and 2,5 pairs of tris(pyrazolyl)methane units on opposite sides of the arene ring.

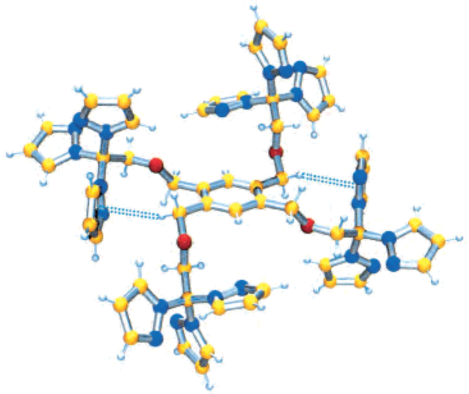
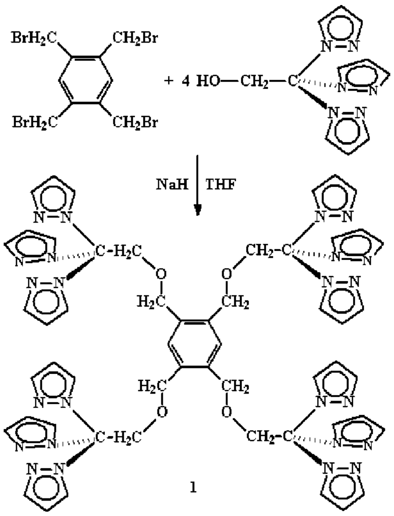


Figure 1. Structure of **1** showing $C-H\cdots\pi$ interactions between two adjacent arms.

Scheme 1. Synthesis of Ligand **1**



The reaction of $AgBF_4$ and **1** in a 2:1 ratio in dry thf yields the coordination polymer $\{1,2,4,5\text{-}C_6H_2[CH_2OCH_2C(pz)_3]_4Ag_2(BF_4)_2\}_n$ (**2**),[5] and its structure has been determined crystallographically.[6] The structure of the basic coordination unit with crystallographic numbering scheme is presented in Figure 2. Each silver(I) is coordinated in a κ^2 fashion to two tris(pyrazolyl)methane groups from two separate ligand molecules in a highly distorted tetrahedral arrangement. The polymeric structure is made up of rings formed by two ligands bonding tris(pyrazolyl)methane groups from nonadjacent positions on the phenyl rings to the same two silver(I) atoms, Figure 3. The holes formed by the large rings are partially occupied by two pyrazolyl rings that are not coordinated to silver(I). This orientation is supported by $C-H\cdots\pi$ interactions between the pyrazolyl rings occupying the holes and methylene hydrogen atoms next to the arene ring with a H−centroid distance of 2.968 Å and with the corresponding

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(2) ES^+/MS for **1**, $[C_{54}H_{54}N_{24}O_4Na]^+$: calcd 1125.4658, found 1125.4657. ^1H NMR (acetone-d_6, 300 Hz): δ 7.61, 7.46 (d of d, 6,6H, 3,5-H pz), 7.04 (s, 1H, C_6H_2), 6.34 (d of d, 6H, 4-H pz), 5.08 (s, 4H, OCH_2Ph), 4.46 (s, 4H, $OCH_2C(pz)_3$).

(3) Crystal data for $C_{54}H_{54}N_{24}O_4$, **1**: fw = 1103.21; monoclinic, space group $I2/a$; $a = 31.4740(17)$ Å; $b = 6.7399(4)$ Å; $c = 25.7722(14)$ Å; $\beta = 100.3340(10)°$; $V = 5378.4(5)$ Å^3; $Z = 4$; $D_c = 1.362$ Mg·m^{-3}; $\mu = 0.093$ mm^{-1}; $F(000) = 2312$; 17060 reflections collected, 5518 independent [R(int) = 0.0399]; final R indices [$I > 2\sigma(I)$] R1 = 0.0546, wR2 = 0.1235.

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(5) ES^+/MS for **2**, $[C_{54}H_{54}N_{24}O_4BF_4Ag_2]^+$: calcd 1403.2900, found 1403.2877. ^1H NMR (acetone-d_6, 300 MHz): δ 7.75, 7.66 (d, d, $J = 1.8$ Hz, 6,6H, 3,5-H pz), 7.40 (s, 1H, C_6H_2), 6.53 (d of d, $J = 1.5$, 6H, 4-H pz), 4.99 (s, 4H, OCH_2Ph), 4.43 (s, 4H, $OCH_2C(pz)_3$).

(6) Crystal data for **2**·$4CH_3CN$: fw = 1656.79; triclinic; space group $P\bar{1}$; $a = 11.4424(19)$ Å; $b = 11.972(2)$ Å; $c = 13.962(2)$ Å; $\alpha = 106.838(3)°$; $\beta = 92.871(3)°$; $\gamma = 100.803(3)°$; $V = 1787.1(5)$ Å^3; $Z = 1$; $D_c = 1.539$ Mg·m^{-3}; $\mu = 0.637$ mm^{-1}; $F(000) = 842$; 12727 reflections collected, 6285 independent [R(int) = 0.0200]; final R indices [$I > 2\sigma(I)$] R1 = 0.0374, wR2 = 0.0977.

10.1021/ic015567a CCC: $20.00

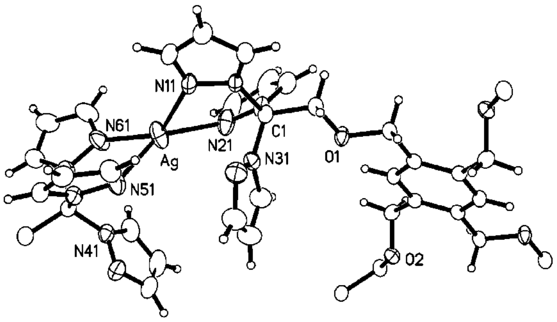

Figure 2. Selected bonds and angles for **2** (Å and deg): Ag−N(11) = 2.403(2); Ag−N(21) = 2.274(2); Ag−N(51) = 2.322(2); Ag−N(61) = 2.315(2); N(11)−Ag−N(21) = 80.60(8); N(21)−Ag−N(61) = 120.33(9); N(21)−Ag−N(51) = 144.78(10); N(51)−Ag−N(61) = 83.03(8); N(11)−Ag−N(61) = 138.74(9); N(11)−Ag−N(51) = 99.03(7).

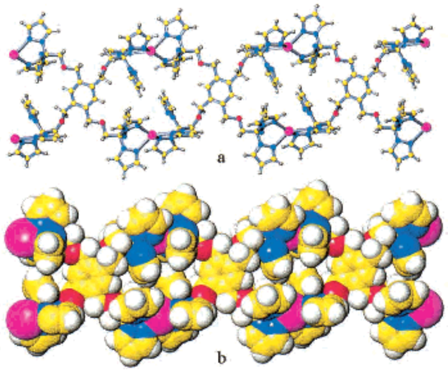

Figure 3. One polymeric strand of **2**: (a) ball-and-stick representation; (b) space-filling representation.

C−centroid distance of 3.654 Å. This interaction is within one arm, as opposed to the "inter-arms" interaction in the free ligand.

The polymeric structure can be regarded also as an infinite chain of 32-atom metallomacrocycles, containing two silver atoms and four κ^2-bonded tris(pyrazolyl)methane units. The distance between two silver atoms in a macrocycle is 9.310 Å and between two equivalent silver atoms from adjacent macrocycles is 14.930 Å. The corresponding Ag−Ag−Ag angles are 87.33° and 92.67°, respectively. Thus, the silver atoms form an infinite chain of almost perfect rectangles.

There are two types of forces that organize the polymer strands into a supramolecular structure. As shown in Figure 4, each BF_4^- makes two C−H···F weak hydrogen bonds. The C−H···F interactions, made between adjacent strands, are 2.398 and 2.484 Å, respectively, with the corresponding angles of 156.19° and 151.11°. While not strong interactions (the sum of van der Waals radii of fluorine and hydrogen atoms, 2.54 Å),[7] the bonds are close to linear. As stated for other types of weak interactions (e.g., weak C−H···O hydrogen bonds), bonds that are close to linear indicate a substantial interaction between the F and H atoms, even in cases when the distances are close to the sum of van der Waals radii.[8,9]

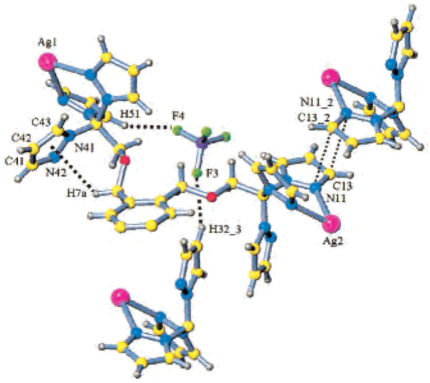

Figure 4. All noncovalent interactions in **2**, including the intrastrand C−H···π interaction of the noncoordinated pyrazolyl ring.

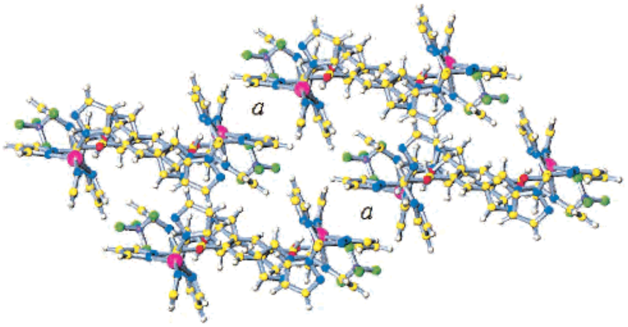

Figure 5. View down the chain direction of four polymer strands. The *a*'s indicate the area of the π−π stacking; solvent molecules are not shown.

As also shown in Figure 4, there are π−π stacking interactions between strands. Although the pyrazolyl rings are displaced with a long centroid−centroid distance of 4.11 Å, the rings are parallel with C−N distances of 3.479 Å. This slippage of aromatic rings involved in π−π interactions is observed frequently, and 3.479 Å is a short distance for this type of interaction.[10,11] In this configuration, an important contribution to the attractive forces arises from a pronounced π−σ attraction interaction of the C13−H σ bonds with the adjacent aromatic π cloud.[10]

Figure 5 shows the crystal packing of four polymeric strands, viewed down the polymer chain of the strands. In this orientation, the π−π stacking interactions are arranged vertically (indicated by *a* in the figure). The C−H···F interactions are between the strands in the figure oriented in the opposite diagonal direction than those involved in π−π stacking. These two types of weak intermolecular interactions support the unusual 3D architecture of **2**.

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Supporting Information Available: Two X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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