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Structural Impact of Multitopic Third-Generation Bis(1-pyrazolyl)methane Ligands: Double, Mononuclear Metallacyclic Silver(I) Complexes

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The reaction of 1,2,4,5-tetrakis(bromomethyl)benzene and hexakis(bromomethyl)benzene with the alkoxide of 2,2-bis(1-pyrazolyl)ethanol leads to the synthesis of the new polytopic ligands 1,2,4,5-$C_6H_2[CH_2OCH_2CH(pz)_2]_4$ ($\mathbf{L_{tetra}}$, pz = pyrazolyl ring) and $C_6[CH_2OCH_2CH(pz)_2]_6$ ($\mathbf{L_{hexa}}$). Reactions of these ligands and the appropriate silver(I) salt lead to the preparation of $[Ag_2\mathbf{L_{tetra}}](BF_4)_2$ (**1**), $[Ag_2\mathbf{L_{tetra}}](SO_3CF_3)_2$ (**2**), $[Ag_3\mathbf{L_{hexa}}](BF_4)_3$ (**3**), and $[Ag_3\mathbf{L_{hexa}}](ClO_4)_3$ (**4**). The solid-state structures of four different complexes crystallized from solutions of **1** or **2** yield five independent structures of the $[Ag_2\mathbf{L_{tetra}}]^{2+}$ cation, all with similar structures. In all of the structures, two *para*-oriented pairs of "arms" ($-CH_2OCH_2CH(pz)_2$) from a single ligand each chelate a silver(I) ion on the opposite sides of the arene ring, forming a double, mononuclear metallacyclic structure of two 17-membered rings connected by the central arene ring. The structures about the silver(I) cations in these complexes are distorted tetrahedral. The flexibility of the ligand leads to two types of arrangements of the linking arms in the five complexes. The central cations of the two L_{hexa} complexes also form double, mononuclear metallacycles, but the structures are different from those of the silver complexes of $\mathbf{L_{tetra}}$ in that both $\mathbf{L_{hexa}}$ cations contain one *para*-linked and one *meta*-linked metallacycle, thus forming a 16- and a 17-membered ring. In addition, the two remaining arms on $\mathbf{L_{hexa}}$ coordinate with additional silver(I) cations, linking the double, mononuclear metallacycles into a coordination polymer network.

Introduction

Self-assembled coordination networks comprised of multidentate ligands and metal ions have interesting properties that are dependent on molecular and supramolecular structure.[1] These properties include porosity,[2] magnetism,[3] and nonlinear optical behavior.[4] In order to design materials with particular properties, the forces that control the organization of the coordination network need to be understood. To this end, systematic studies have been carried out that show ligand topicity, the flexibility of the linker groups joining the coordination sites, and the coordination preferences of the metal all have a strong influence on the architecture of the coordination network.[5] Noncovalent interactions, such as hydrogen bonding and $\pi-\pi$ interactions, also influence the coordination network and the supramolecular structure.[6] The structures can also be influenced by the covalent and noncovalent interactions involving the anions and solvent.[7]

Our efforts in this area started with the syntheses of multitopic ligands built from tris(1-pyrazolyl)methane units of the general formula $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$ (n = 2, 3, 4, and 6, pz = pyrazolyl ring).[8] We have designated these ligands as "third generation", ligands functionalized at the noncoordinating "back" position away from the metal center. Third-generation ligands can introduce functional groups with specific physical properties or that form strong noncovalent interactions.[9] Multitopic third-generation

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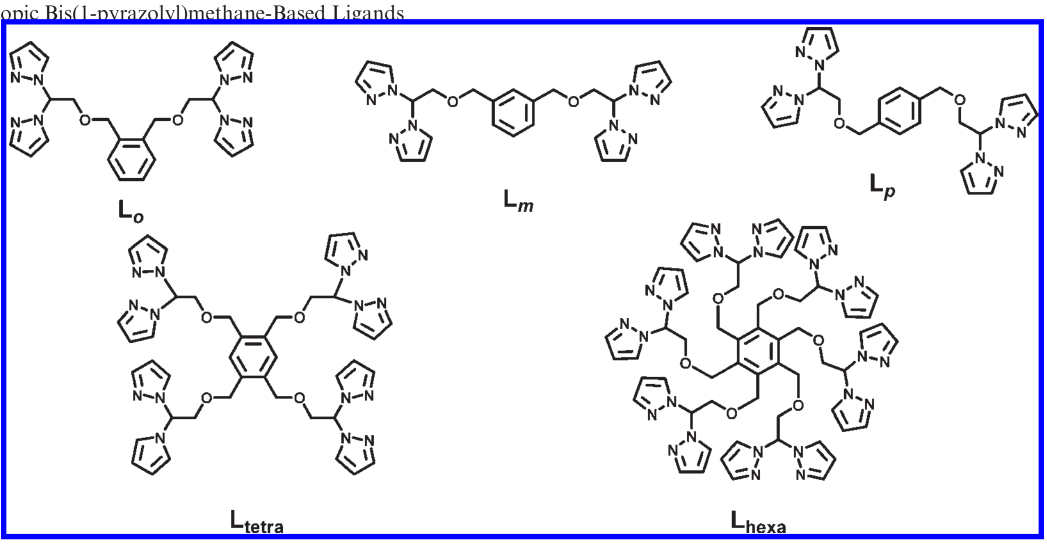
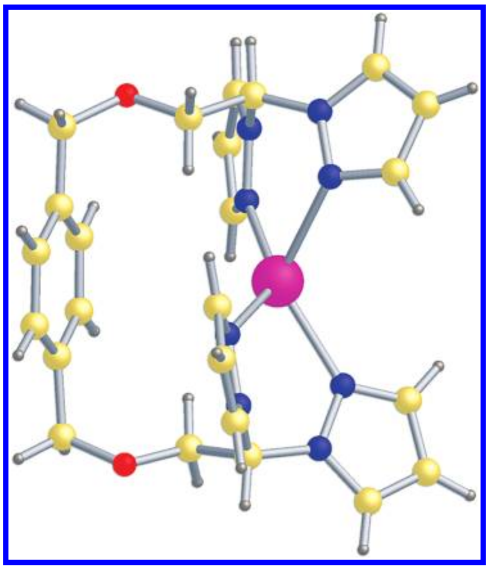
Chart 1. Multitopic Bis(1-pyrazolyl)methane-Based Ligands



ligands can also be prepared that control the directional orientation of the poly(pyrazolyl)methane units by selective substitution of a central aromatic ring or other central building block.[8,10,11]

An interesting finding about the self-assembly processes for silver(I) complexes of the tris(pyrazolyl)methane-based ligands was the domination of the $\kappa^2-\kappa^1$ coordination mode that supported complex polymeric structures. More recently, we have systematically expanded this family of multitopic ligands to include the ditopic ligands built from bis(1-pyrazolyl)methane units, *ortho*-, *meta*-, and *para*-$C_6H_4[CH_2OCH_2CH(pz)_2]_2$; see Chart 1.[11] These new bis(1-pyrazolyl)methane ligands were synthesized in order to determine the coordination preferences of ligands that cannot enter into the $\kappa^2-\kappa^1$ coordination mode observed with the tris(pyrazolyl)methane-based analogues. In our initial work, we found that silver(I) complexes of *ortho*-linked ligands built from either bis(1-pyrazolyl)methane ligands or tris(1-pyrazolyl)methane units formed similar coordination polymers.[11a] However, the silver(I) complexes of *meta*- and *para*-linked ligands did not form coordination polymers, the dominant structure also seen in the silver(I) complexes of *meta*- and *para*-linked ligands containing tris(1-pyrazolyl)methane units. In contrast, the *meta*- and *para*-linked ligands with bis(1-pyrazolyl)methane units chelate a single silver(I) ion to form mononuclear metallacyles, Chart 2.[11b] These mononuclear metallacycles have a unique ring size containing 16 or 17 members, which is much larger than typically found in coordination compounds.

Chart 2. Cationic *para*-Linked Mononuclear Metallacycle



Because of the uniqueness of the mononuclear metallacyclic structures formed by the *meta*- and *para*-linked ligands built from bis(1-pyrazolyl)methane units, we have synthesized the analogous tetratopic and hexatopic ligands,

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$\mathbf{L_{tetra}}$ and $\mathbf{L_{hexa}}$, shown in Chart 1. These ligands have the potential to form a new type of structure where two mononuclear metallacycles form from a single ligand, one on each side of the arene ring. Assuming the formation of this type of structure, another interesting question that arises with these ligands is whether *meta*-linked or *para*-linked metallacycles will form, as both are possible. We report here the syntheses and structures of the silver(I) complexes of these tetratopic and hexatopic ligands containing bis(1-pyrazolyl)methane coordination units.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere using standard Schlenk techniques and a Vacuum Atmospheres HE-493 drybox. The tetrahydrofuran was dried and distilled prior to use following standard techniques. Other solvents were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury/VX 300 or Varian Mercury/VX 400. Proton chemical shifts are reported in ppm and were referenced to nondeuterated solvent signals (^{1}H) or deuterated solvent signals (^{13}C). Assignments of ^{13}C shifts in compounds containing 1,2,4,5-$C_6H_2[CH_2OCH_2CH(pz)_2]_4$ were confirmed by gradient heteronuclear multiple quantum coherence or gradient heteronuclear multiple-bond correlation 2D experiments. Elemental analyses were performed by Robertson Microlit Laboratories (Madison, NJ). The 2,2′-bis(1-pyrazolyl)ethanol was prepared following the published method.[11a] Silver tetrafluoroborate, silver perchlorate, silver trifluoromethanesulfonate, 1,2,4,5-tetrakis(bromomethyl)benzene, and hexakis(bromomethyl)benzene were obtained from commercial sources (Aldrich) and used as received.

Synthesis of 1,2,4,5-$C_6H_2[CH_2OCH_2CH(pz)_2]_4$ (L_{tetra}). NaH (0.229 g, 9.54 mmol) was suspended in 200 mL of dry tetahydrofuran (THF) in a 500 mL three-neck, round-bottom flask fitted with an addition funnel and a vacuum adapter. Against a stream of N_2, 2,2′-bis(1-pyrazolyl)ethanol (1.70 g, 9.54 mmol) was added to the suspension all at once and gas evolution was noted. A condenser was fitted on the three-neck flask and the mixture stirred and heated at reflux for 45 min, during which time the mixture became a pale yellow solution. To the refluxing solution was added dropwise a solution of 1,2,4,5-tetrakis(bromomethyl)benzene (1.07 g, 2.38 mmol) in 25 mL of THF over 30 min. During this time a white precipitate formed and the color changed from a pale yellow to dark yellow and finally to orange. The reaction was heated at reflux for 72 h and cooled to room temperature, and 100 mL of water and 100 mL of diethyl ether were added. The two phases were separated and the aqueous layer was extracted with diethyl ether (3 × 100 mL). The combined organic layer was washed with 100 mL of brine. The organic layer was then dried with $MgSO_4$ and filtered, and the solvent evaporated *in vacuo* to give 2.48 g of yellow powder, pure by ^{1}H NMR (88%). For elemental analysis the yellow powder (0.300 g) was stirred in 35 mL of boiling ethanol, filtered while hot through filter paper, and allowed to cool. The yellow crystals that formed were collected and dried *in vacuo*, yielding 0.083 g of $\mathbf{L_{tetra}}$. Mp: 153−154 °C. Anal. Calcd for $C_{42}H_{46}N_{16}O_4$: C, 60.13; H, 5.53; N, 26.71. Found: C, 59.79; H, 5.52; N, 26.00. ^{1}H NMR (400 Mz, CD_3CN): δ 7.75, 7.49 (d, d, J = 2.0 Hz, J = 1.6 Hz, 8 H, 8 H, 3,5-H-pz), 7.03 (s, 2 H, arene), 6.65 (t, J = 7.0 Hz, 4 H, CH(pz)$_2$), 6.27 (d, J = 2.0 Hz, 8 H, 4-H-pz), 4.38 (s, 8 H, ArCH_2), 4.34 (d, J = 6.8 Hz, 8 H, OCH_2CH). ^{13}C NMR (400 Hz, CD_3CN): 140.1, 129.4 (3,5-C-pz), 135.8 (CH-arene), 129.4 (C-arene), 106.3 (4-C-pz), 73.5 (OCH$_2$$C$H), 70.1 (Ar$CH_2$), 69.1 (O$CH_2$CH). MS ESI(+) m/z (rel % abund) [assgn]: 877 (13) $[\mathbf{L_{tetra}} + K]^+$, 862 (88) $[\mathbf{L_{tetra}} + Na]^+$, 839 (100) $[\mathbf{L_{tetra}} + H]^+$.

Synthesis of $C_6[CH_2OCH_2CH(pz)_2]_6$ (L_{hexa}). In a 500 mL Schlenk flask, NaH (0.128 g, 5.33 mmol) was suspended in 250 mL of dry THF. Against a stream of N_2, 2,2′-bis(1-pyrazolyl)ethanol (0.949 g, 5.33 mmol) was added to the suspension all at once and gas evolution was noted. The mixture was stirred for 1 h, during which time the reaction became clear. The hexakis(bromomethyl)benzene was added all at once against a stream of nitrogen and the reaction heated at reflux for 24 h, during which time a white precipitate formed. The reaction was allowed to cool, and 100 mL of water was added. The resulting solution was extracted with dichloromethane (3 × 100 mL). The combined organic phase was dried with $MgSO_4$ and filtered, and the solvent removed *in vacuo*. The resulting solid was stirred in ether (200 mL) for 4 h to remove residual 2,2′-bis(1-pyrazolyl)ethanol and then filtered to give 0.709 g (71%) of $\mathbf{L_{hexa}}$. Mp: 168−170 °C. ^{1}H NMR (400 Hz, $(CD_3)_2SO$): δ 8.01, 7.53 (d, d, J = 2.4 Hz, J = 1.6 Hz, 12 H, 12 H, 3,5-H-pz), 6.83 (t, J = 7.2 Hz, 6 H, CH(pz)$_2$), 6.31 (t, J = 2.0 Hz, 12 H, 4-H-pz), 4.43 (d, J = 6.8 Hz, 12 H, OCH_2CH), 4.12 (s, 12 H, ArCH_2). ^{13}C NMR ($(CD_3)_2SO$): δ 139.8 (pz), 136.9 (arene), 129.7 (pz) 106.2 (pz), 72.3, 69.3, 65.2. MS ESI(+) m/z (rel % abund) [assgn]: 1257 (14) $[\mathbf{L_{hexa}} + K]^+$, 1242 (100) $[\mathbf{L_{hexa}} + Na]^+$, 1220 (21) $[\mathbf{L_{hexa}} + H]^+$, 610 (18) $[\mathbf{L_{hexa}} + 2H]^{2+}$. HRMS: ES$^+$ (m/z): $[\mathbf{L_{hexa}} + H]^+$ calcd for $[C_{60}H_{67}N_{24}O_6]^+$ 1219.5675; found 1219.5645.

Synthesis of $[Ag_2\{1,2,4,5\text{-}C_6H_2[CH_2OCH_2CH(pz)_2]_4\}](BF_4)_2$ (1). The powder sample of $\mathbf{L_{tetra}}$ (0.273 g, 0.33 mmol) was dissolved in 50 mL of THF. $AgBF_4$ (0.127 g, 0.65 mmol) was dissolved in 5 mL of THF and cannulated into the solution of $\mathbf{L_{tetra}}$. A white precipitate formed immediately, the flask was wrapped in foil, and the mixture was allowed to stir for 12 h. The precipitate was cannula filtered and washed with 5 mL of THF, and the pale yellow solid dried *in vacuo* overnight, yielding 0.226 g (57%) of **1**. Dec: 152−159 °C. ^{1}H NMR (400 Mz, CD_3CN): δ 7.92, 7.42 (d, d, J = 2.0 Hz, J = 2.0 Hz, 8 H, 8 H, 3, 5-H-pz), 6.88 (s, 2 H, arene), 6.69 (t, J = 7.2 Hz, 4 H, CH(pz)$_2$), 6.27 (d, J = 2.0 Hz, 8H, 4-H-pz), 4.19 (d, J = 7.2 Hz, 8 H, ArCH_2), 3.97 (s, 8 H, OCH_2CH). ^{13}C NMR (400 Hz, CD_3CN): 143.1, 133.2 (3, 5-C-pz), 136.4 (CH-arene), 134.8 (C-arene), 106.9 (4-C-pz), 72.6 (OCH$_2$$C$H), 69.6 (Ar$CH_2$), 66.3 (O$CH_2$CH). MS ESI(+) m/z (rel % abund) [assgn]: 1141 (2) $[\mathbf{L_{tetra}}Ag_2(BF_4)]^+$, 947 (100) $[\mathbf{L_{tetra}}Ag]^+$, 527 (100) $[\mathbf{L_{tetra}}Ag_2]^{2+}$. HRMS: ES$^+$ (m/z): $[\mathbf{L_{tetra}}Ag_2(BF_4)]^+$ calcd for $[C_{42}H_{46}Ag_2N_{16}O_4BF_4]^+$ 1141.2026; found 1141.1997.

Single crystals used in the X-ray studies were grown by vapor diffusion of Et_2O into 1 mL of an 8.14 mmol solution of **1** in acetonitrile. A mixture of two kinds of single crystals grew, which could be visually distinguished by their crystal habit and were identified by X-ray crystallography studies as $[Ag_2\mathbf{L_{tetra}}](BF_4)_2\cdot(CH_3CN)\cdot(solv)$ (**1a**, blocklike habit) and $\{[Ag_2\mathbf{L_{tetra}}](BF_4)_2\}_3[Ag(CH_3CN)_3(BF_4)]_2$ (**1b**, needle habit) by X-ray crystallography.

Synthesis of $[Ag_2\{1,2,4,5\text{-}C_6H_2[CH_2OCH_2CH(pz)_2]_4\}](SO_3CF_3)_2$ (2). The powder sample of $\mathbf{L_{tetra}}$ (0.248 g, 0.30 mmol) was added to a 250 mL Schlenk flask containing 100 mL of THF followed by the addition of $AgSO_3CF_3$ (0.152 g, 0.59 mmol) against a stream of N_2. The flask was quickly capped and wrapped in foil. The reaction was stirred for 18 h, during which time a precipitate formed. The system was cannula filtered and the solid washed with 5 mL of THF. The off-white solid was dried *in vacuo* overnight, yielding 0.167 g (42%) of **2**. Dec: 130−135 °C. Single crystals suitable for X-ray studies were grown by vapor diffusion of Et_2O into 1 mL of a 3.7 mmol solution of **2** in acetonitrile. A mixture of two kinds of single crystals grew from the acetonitrile solution of **2**, which were identified by X-ray crystallography studies as $[Ag_2\mathbf{L_{tetra}}](SO_3CF_3)_2\cdot 2CH_3CN$ (**2a**, square block habit) and $[Ag_2\mathbf{L_{tetra}}](SO_3CF_3)_2\cdot 2(CH_3CN)\cdot 0.5(C_4H_{10}O)$ (**2b**, needle habit). Crystals (a mixture of **2a** and **2b**) used for elemental analysis were removed from the mother liquor, rinsed with diethyl ether, and dried *in vacuo*, which resulted in the loss of solvent of crystallization. Anal. Calcd for $C_{44}H_{46}Ag_2N_{16}O_{10}S_2$: C, 39.07; H, 3.43; N, 16.57.

Found: C, 38.88; H, 3.52; N, 16.26. ^{1}H NMR (300 Hz, CD_3CN): δ 7.90, 7.43 (d, d, J = 2.7 Hz, J = 1.8 Hz, 8 H, 8 H, 3,5-*H*-pz), 6.88 (s, 2 H, arene), 6.68 (t, J = 7.2 Hz, 4 H, C*H*(pz)$_2$), 6.37 (t, J = 2.1 Hz, 8 H, 4-*H*-pz), 4.21 (d, J = 6.9 Hz, 8 H, OC*H*$_2$CH) 4.03 (s, 8 H, ArC*H*$_2$). ^{13}C NMR (400 Hz, CD_3CN): δ 142.6, 132.7 (3,5-*C*-pz), 135.9 (*C*H-arene), 134.3 (*C*-arene), 106.5 (4-*C*-pz), 72.2 (OCH$_2$*C*H), 69.1 (Ar*C*H$_2$), 65.9 (O*C*H$_2$CH). MS ESI(+) *m*/*z* (rel % abund) [assgn]: 1203 (1) $[\mathbf{L_{tetra}}Ag_2(SO_3CF_3)]^+$, 947 (1) $[\mathbf{L_{tetra}}Ag]^+$, 527 (100) $[\mathbf{L_{tetra}}Ag_2]^{2+}$.

Synthesis of $\{[\mathbf{Ag_3\{C_6[CH_2OCH_2CH(pz)_2]_6\}](BF_4)_3}\}_n$ **(3).** $\mathbf{L_{hexa}}$ (0.122 g, 0.10 mmol) was partially dissolved in 180 mL of acetonitrile. $AgBF_4$ (0.058 g, 0.30 mmol) was dissolved in 20 mL of acetonitrile and cannulated into the $\mathbf{L_{hexa}}$ suspension. The reaction flask was wrapped in foil and allowed to stir for 4 h, during which time it became a clear solution. The solvent was removed *in vacuo* to obtain 0.073 g of an off-white solid. Dec: 129−136 °C. Single crystals suitable for X-ray studies were grown by vapor diffusion of Et_2O into 1 mL of a 1.2 mmol solution of **3** in acetonitrile. The crystals taken directly from the mother liquor were identified as $\{[Ag_3\mathbf{L_{hexa}}](BF_4)_3\cdot(C_4H_{10}O)\cdot 5(CH_3CN)\}_n$ (**3a**). Crystals used for elemental analysis were removed from the mother liquor, rinsed with diethyl ether, and dried *in vacuo*, which resulted in the loss of solvent of crystallization. Anal. Calcd for $C_{60}H_{66}Ag_3B_3F_{12}N_{24}O_6$: C, 39.96; H, 3.69; N, 18.64. Found: C, 39.49; H, 3.77; N, 18.56. ^{1}H NMR (300 Hz, CD_3CN): δ 7.86, 7.39 (d, d, J = 2.1 Hz, J = 2.1 Hz, 12 H, 12 H, 3,5-*H*-pz), 6.69 (t, J = 7.2 Hz, 6 H, C*H*(pz)$_2$), 6.34 (t, J = 2.1 Hz, 12 H, 4-*H*-pz), 4.25 (d, J = 7.2 Hz, 12 H, OC*H*$_2$CH) 4.15 (s, 12 H, ArC*H*$_2$). ^{13}C NMR (CD_3CN): δ 142.8 (pz), 137.8 (arene), 132.4 (pz) 107.0 (pz), 72.8, 67.7, 65.4. MS ESI(+) *m*/*z* (rel % abund) [assgn]: 1327.5 (18) $[\mathbf{L_{hexa}}Ag]^+$, 1219.6 (5) $[\mathbf{L_{hexa}} + H]^+$, 717.2 (100) $[\mathbf{L_{hexa}}Ag_2]^{2+}$. HRMS: ES$^+$ (*m*/*z*): $[\mathbf{L_{hexa}}Ag]^+$ calcd for $[C_{60}H_{66}{}^{107}AgN_{24}O_6]^+$ 1325.4648; found 1325.4595.

Synthesis of $\{[\mathbf{Ag_3\{C_6[CH_2OCH_2CH(pz)_2]_6\}](ClO_4)_3}\}_n$ **(4).** $\mathbf{L_{hexa}}$ (0.122 g, 0.10 mmol) was partially dissolved in 50 mL of acetonitrile. $AgClO_4$ (0.062 g, 0.30 mmol) was dissolved in 10 mL of acetonitrile and cannulated into the $\mathbf{L_{hexa}}$ suspension. The reaction flask was wrapped in foil and allowed to stir for 2.5 h, during which time it became a clear solution. The solvent was removed *in vacuo* to obtain 0.143 g of an off-white solid of **4**. Dec: 155−168 °C. Single crystals suitable for X-ray studies and elemental analysis were grown by vapor diffusion of Et_2O into 1.1 mL of a 78 mmol solution of **4** in acetonitrile. The crystals taken directly from the mother liquor were identified as $\{[Ag_3\mathbf{L_{hexa}}](ClO_4)_3\cdot 2(CH_3CN)\cdot(solv)\}_n$ (**4a**). Crystals used for elemental analysis were removed from the mother liquor, rinsed with diethyl ether, and dried *in vacuo*, which resulted in the loss of solvent of crystallization. Anal. Calcd for $C_{60}H_{66}Ag_3Cl_3N_{24}O_{18}$: C, 39.14; H, 3.61; N, 18.26. Found: C, 38.48; H, 3.46; N, 17.80. ^{1}H NMR (400 Hz, CD_3CN): δ 7.86, 7.40 (d, d, J = 2.8 Hz, J = 2.8 Hz, 12 H, 12 H, 3,5-*H*-pz), 6.69 (t, J = 7.2 Hz, 6 H, C*H*(pz)$_2$), 6.34 (t, J = 2.0 Hz, 12 H, 4-*H*-pz), 4.24 (d, J = 7.2 Hz, 12 H, OC*H*$_2$CH), 4.15 (s, 12 H, ArC*H*$_2$). ^{13}C NMR (CD_3CN): δ 142.6 (pz), 137.5 (arene), 132.2 (pz), 106.8 (pz), 72.58, 67.4, 65.2. MS ESI(+) *m*/*z* (rel % abund) [assgn]: 1327 (38) $[\mathbf{L_{hexa}}Ag]^+$, 1220 (100) $[\mathbf{L_{hexa}} + H]^+$, 717 (51) $[\mathbf{L_{hexa}}Ag_2]^{2+}$, 664 (39) $[\mathbf{L_{hexa}}Ag + H]^{2+}$. HRMS: ES$^+$ (*m*/*z*): $[\mathbf{L_{hexa}}Ag_2]^{2+}$ calcd for $[C_{60}H_{66}Ag_2N_{24}O_6]^{2+}$ 716.1818; found 716.1844.

Crystallography. X-ray diffraction intensity data for each complex were measured at 150(1) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, λ = 0.71073 Å).[12] Raw area detector data frame reduction was performed with the SAINT+ program.[12] Final unit cell parameters were determined by least-squares refinement of large sets of reflections from each data set. Direct methods structure solution, difference Fourier calculations, and full-matrix least-squares refinement against F^2 were performed with the SHELXTL suite of programs.[13] Non-hydrogen atoms were refined with anisotropic displacement parameters, except for those affected by disorder (isotropic). Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. The Squeeze program implemented in PLATON was used to account for the contribution of some severely disordered species to the structure factors in compounds **1a** and **4a**.[14] A summary of crystal data and refinement statistics for each complex is listed in Table 1. Full details of each refinement are found in the Supporting Information.

Results

Synthesis and Characterization. The synthesis of 1,2,4,5-$C_6H_2[CH_2OCH_2CH(pz)_2]_4$ ($\mathbf{L_{tetra}}$) was carried out by adding 2,2-bis(1-pyrazolyl)ethanol to a suspension of sodium hydride in tetrahydrofuran, followed by the dropwise addition of 1,2,4,5-tetrakis(bromomethyl)benzene to this mixture being heated at reflux. The synthesis of $C_6[CH_2OCH_2CH(pz)_2]_6$ ($\mathbf{L_{hexa}}$) is similar to that of $\mathbf{L_{tetra}}$.

The silver(I) complexes of $\mathbf{L_{tetra}}$ were prepared by combining the ligand with 2 equiv of either $AgBF_4$ or $AgSO_3CF_3$ to give $[Ag_2\mathbf{L_{tetra}}](BF_4)_2$ (**1**) or $[Ag_2\mathbf{L_{tetra}}](SO_3CF_3)_2$ (**2**), respectively. Complex **1** was also synthesized by combining the ligand and 4 equiv of $AgBF_4$, indicating that the metal stoichiometry does not influence the product. The silver(I) complexes of $\mathbf{L_{hexa}}$ were prepared by combining the ligand with 3 equiv of $AgBF_4$ or $AgClO_4$ to give $[Ag_3\mathbf{L_{hexa}}](BF_4)_3$ (**3**) or $[Ag_3\ \mathbf{L_{hexa}}](ClO_4)_3$ (**4**), respectively. In order to grow crystals of these solids, the silver complexes **1**−**4** were dissolved in acetonitrile, and diethyl ether was allowed to diffuse into 1 mL portions of the resulting solutions. From the solution of **1**, a mixture of two kinds of single crystals grew, which could be visually distinguished by their crystal habit and were identified by X-ray crystallography studies as $[Ag_2\mathbf{L_{tetra}}](BF_4)_2\cdot(CH_3CN)\cdot(solv)$ (**1a**, solv = unknown solvent in the crystal lattice) and $\{[Ag_2\mathbf{L_{tetra}}](BF_4)_2\}_3[Ag(CH_3CN)_3(BF_4)]_2$ (**1b**). A mixture of two kinds of single crystals also grew from the acetonitrile solution of **2** and were identified by X-ray crystallography studies as $[Ag_2\mathbf{L_{tetra}}](SO_3CF_3)_2\cdot 2CH_3CN$ (**2a**) and $[Ag_2\mathbf{L_{tetra}}](SO_3CF_3)_2\cdot 2(CH_3CN)\cdot 0.5(C_4H_{10}O)$ (**2b**). The crystals grown from solutions of **3** and **4** were identified by X-ray crystallography as $\{[Ag_3\mathbf{L_{hexa}}](BF_4)_3\cdot(C_4H_{10}O)\cdot 5(CH_3CN)\}_n$ (**3a**) and $\{[Ag_3\mathbf{L_{hexa}}](ClO_4)_3\cdot 2(CH_3CN)\cdot(solv)\}_n$ (**4a**), respectively. The silver(I) complex made from $\mathbf{L_{hexa}}$ and $AgSO_3CF_3$ did not produce crystals suitable for X-ray crystallography studies and was not studied further. The new compounds are off-white solids that are air stable, but are light sensitive in acetonitrile solutions. Although the solids of these compounds are less light sensitive than in solution, they were stored in foil-wrapped vials to delay decomposition.

The ^{1}H NMR spectra of the all silver(I) complexes containing $\mathbf{L_{tetra}}$ in acetonitrile are clearly different from the free ligands, showing that this coordinating solvent does not displace the bis(1-pyrazolyl)methane units from coordination to silver(I). Due to solubility issues, the ^{1}H

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(12) *SMART*, version 5.625, *SAINT+*, version 6.45; Bruker Analytical X-ray Systems, Inc.: Madison, WI, **2001**.

(13) *SHELXTL*, version 6.14; Bruker Analytical X-ray Systems, Inc.: Madison, WI, **2000**.

(14) Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool; Utrecht University: Utrecht, The Netherlands, **1998**.

Table 1. Selected Crystal Data and Refinement Details

	1a	**1b**	**2a**	**2b**	**3a**	**4a**
formula	$C_{44}H_{49}Ag_2B_2$-$F_8N_{17}O_4$	$C_{138}H_{156}Ag_8B_8$-$F_{32}N_{54}O_{12}$	$C_{48}H_{52}Ag_2F_6$-$N_{18}O_{10}S_2$	$C_{48}H_{54}Ag_2F_6$-$N_{17}O_{10.50}S_2$	$C_{74}H_{91}Ag_3B_3$-$F_{12}N_{29}O_7$	$C_{64}H_{72}Ag_3C_{13}$ $N_{26}O_{18}$
fw, g mol^{-1}	1269.36	4320.61	1434.94	1430.94	2082.8	1923.44
cryst syst	orthorhombic	trigonal	monoclinic	monoclinic	triclinic	triclinic
space group	$C222_1$[a]	$P\bar{3}c1$	$P2/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
T, K	150(1)	150(1)	150(1)	150(1)	150(1)	150(2)
a, Å	19.0729(8)	24.7918(4)	20.8927(18)	11.5968(11)	13.7323(6)	13.8076(6)
b, Å	21.6099(9)	24.7918(4)	13.8500(12)	38.086(4)	15.3482(6)	16.0102(7)
c, Å	27.5003(11)	16.0672(5)	20.9026(18)	13.9258(14)	24.6125(10)	24.8007(11)
α, deg	90	90	90	90	100.249(1)	77.791(1)
β, deg	90	90	96.064(2)	101.843(2)	97.538(1)	86.827(1)
γ, deg	90	120	90	90	115.024(1)	65.033(1)
V, Å^3	11334.6(8)	8552.4(3)	6014.6(9)	6019.7(10)	4499.8(3)	4854.2(4)
Z	8	2	4	4	2	2
R1 ($I > 2\sigma(I)$)[b]	0.0505	0.0365	0.0398	0.0606	0.0491	0.0497
wR2 ($I > 2\sigma(I)$)[b]	0.1200	0.1000	0.1049	0.1596	0.1035	0.1159

[a] Flack parameter (**1a**) = 0.04(3). [b] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

NMR and ^{13}C NMR spectra of $\mathbf{L}_{\mathbf{hexa}}$ were not run in acetonitrile, so comparisons between the silver complexes and the free ligand in acetonitrile cannot be made. In our previous studies of silver(I) complexes of bis(1-pyrazolyl)-methane ligands, acetonitrile does not displace the bis-(1-pyrazolyl)methane units;[9a,10,11] however acetonitrile does displace ligands built on tris(1-pyrazolyl)methane units.[8g,h] For all complexes, although the X-ray structures show that in the solid state the pyrazolyl rings are non-equivalent (*vide infra*), the NMR spectra show equivalent rings, presumably because of fast exchange of the ligands on the NMR time scale. The spectra of **1** and **2** are essentially identical, as are the spectra of **3** and **4**. This result suggests that the cationic species present in solution are anion independent. Electrospray mass spectroscopy of **1** and **2** shows peaks corresponding to $[\mathbf{L}_{\mathbf{tetra}}Ag_2]^{2+}$ and $[\mathbf{L}_{\mathbf{tetra}}Ag]^+$ for both, $[\mathbf{L}_{\mathbf{tetra}}Ag_2(BF_4)]^+$ for **1**, and $[\mathbf{L}_{\mathbf{tetra}}Ag_2(SO_3CF_3)]^+$ for **2**. Electrospray mass spectroscopy of **3** and **4** shows peaks for both $[\mathbf{L}_{\mathbf{hexa}}Ag]^+$ and $[\mathbf{L}_{\mathbf{hexa}}Ag_2\,]^{2+}$.

Solid-State Structures of Silver Complexes of 1,2,4,5-$\mathbf{C_6H_2[CH_2OCH_2CH(pz)_2]_4}$. The silver(I) complexes $[Ag_2\mathbf{L}_{\mathbf{tetra}}](BF_4)_2\cdot(CH_3CN)\cdot$(solv) (**1a**), $\{[Ag_2\mathbf{L}_{\mathbf{tetra}}](BF_4)_2\}_3[Ag(CH_3CN)_3(BF_4)]_2$ (**1b**), $[Ag_2\mathbf{L}_{\mathbf{tetra}}](SO_3CF_3)_2\cdot 2CH_3CN$ (**2a**), and $[Ag_2\mathbf{L}_{\mathbf{tetra}}](SO_3CF_3)_2\cdot 2(CH_3CN)\cdot 0.5(C_4H_{10}O)$ (**2b**) all have very similar monomeric cationic units, regardless of counterions or solvent present; see Tables S1 and S2 for important bond distances and angles about the four-coordinate silver(I) cations in the Supporting Information. Complexes **1a** and **2b** each have one crystallographically independent cationic unit with no imposed symmetry equivalent atoms, Figure 1.

Complex **1b** has one cationic unit (Figure S1), and **2a** has two independent cationic units (Figure S2, see Supporting Information), all of which have crystallographically imposed C_2 point symmetry. The 2-fold axis passes through the silver−silver vector in each of the three cations. In addition to the cationic unit built by the $\mathbf{L}_{\mathbf{tetra}}$ ligand, **1b** has a second cationic unit comprised of three acetonitriles and a tetrafluoroborate coordinating to a silver cation in a distorted tetrahedral environment, where the three angles of the F−Ag−N type are 101° and the three angles of the N−Ag−N type are 117°. Complex **1b** is the only structure to incorporate this extra silver.

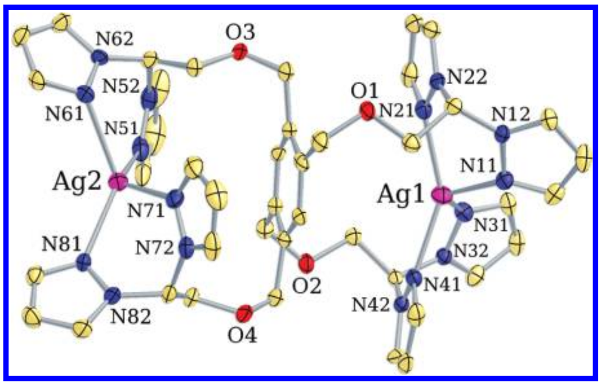

Figure 1. Structure of the cationic unit in $[Ag_2\mathbf{L}_{\mathbf{tetra}}](BF_4)_2\cdot(CH_3CN)\cdot$(solv) (**1a**). Displacement parameters are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

All of the cationic structures are monomeric, containing two 17-membered metallacycles. These metallacyles are formed by two sets of bis(1-pyrazolyl)methane units on two "arms" ($-CH_2OCH_2CH(pz)_2$) from the same ligand, with each pair oriented *para* about the central arene ring, chelating a silver ion on the opposite sides of the ring, forming a *double, mononuclear metallacyclic* structure.

A parameter, τ_4, has been introduced by Houser[15] to describe the geometry of a four-coordinate metal system. This parameter is determined by the following equation:

$$\tau_4 = \frac{360° - (\beta + \alpha)}{141°}$$

where α and β are the largest angles. A perfect square-planar geometry is denoted when τ_4 equals 0, and a perfect tetrahedral geometry is described when τ_4 equals 1. Table 2 lists τ_4 for all the four-coordinate silver ions in **1a**, **1b**, **2a**, and **2b** in the central cationic units. The τ_4 values average 0.58, ranging from 0.51 to 0.72, showing the structures are distorted tetrahedral, where the main distortion is caused by the restricted "bite" angle of the bis(1-pyrazolyl)methane units. This distortion lowers the corresponding N−Ag−N angles, which range from

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(15) Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955.

Table 2. Four-Coordinate τ_4 Parameters

complex	silver	τ_4
1a	Ag(1)	0.61
	Ag(2)	0.69
1b	Ag(1)	0.72
	Ag(2)	0.69
2a	Ag(1)	0.55
	Ag(2)	0.71
	Ag(3)	0.54
	Ag(4)	0.71
2b	Ag(1)	0.62
	Ag(2)	0.51
3a	Ag(1)	0.66
	Ag(2)	0.67
4a	Ag(1)	0.64
	Ag(2)	0.67

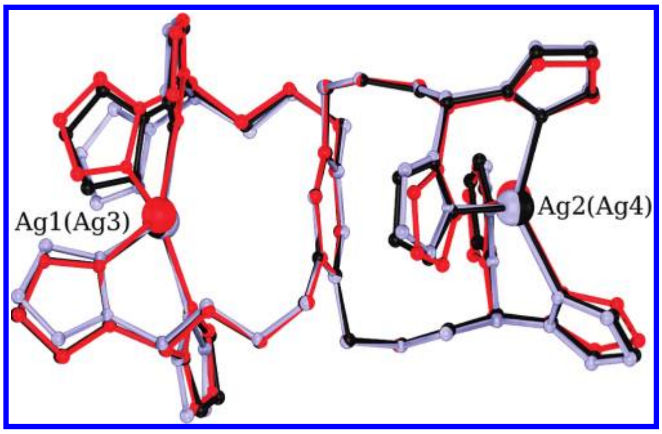

Figure 2. Superimposed images of **1a** shown in blue and **2a** shown in black for cation containing Ag(1) and red for cation containing Ag(3).

82.01° to 86.09°. The nitrogen−silver bond lengths, given in Tables S1 and S2 in the Supporting Information, are within the normal range for these types of compounds.[8b,c,f−i,10,11] The distances between the silver ion and the central arene ring range from 3.95 to 4.61 Å, distances too long to support any silver−arene interactions.[16]

Although the metrics in the tables, all involving the silver cations, are similar in all five cases, there are some notable differences in the arrangement of the linking arms of these silver complexes containing $\mathbf{L_{tetra}}$. Such a comparison of the five metallacyclic cationic units shows similarities among the three cations of **1a** and **2a** and between the two cations of **1b** and **2b**, but the two types have differences. Figure 2 shows the overlay of the cations of **1a** (shown in blue) and **2a** (shown in black for cation containing Ag(1) and red for cation containing Ag(3)). Figure 3 shows the superimposed images of the second set of cations; the cation from **1b** is shown in red, and the cation in **2b** is shown in black.

Comparisons between the two groups show that the major differences in the two types are the orientations of the CH_2OCH_2 chain and the pyrazolyl rings. Two side-by-side comparisons of the cations in **1a** and **1b** viewed at two different orientations, one at right angles to the other, are depicted in Figure 4. Comparing Figure 4, parts a and b, shows that the orientations of the CH_2OCH_2 chains on the left sides of the arene rings are similar. However, the orientations of the CH_2OCH_2 chains on the right sides of the arene rings differ. Figure 4, parts c and d, shows the cations of **1a** and **1b** viewed down the silver cations, where the differences in the orientations of the pyrazolyl rings are exemplified. Clearly, the flexibility of the ligand allows for variations among the cations, while retaining the main double, mononuclear metallacyclic structure.

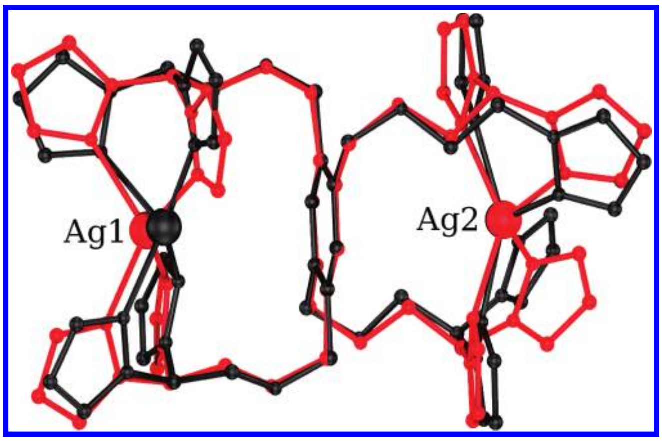

Figure 3. Superimposed images of **1b** shown in red and **2b** shown in black.

Solid-State Structures of Silver Complexes of $\mathbf{C_6[CH_2OCH_2CH(pz)_2]_6}$. The silver(I) complexes containing $\mathbf{L_{hexa}}$, $\{[Ag_3\mathbf{L_{hexa}}](BF_4)_3\cdot(C_4H_{10}O)\cdot 5(CH_3CN)\}_n$ (**3a**) and $\{[Ag_3\mathbf{L_{hexa}}](ClO_4)_3\cdot 2(CH_3CN)\cdot(solv)\}_n$ (**4a**), have a similar central cationic structure, which can be seen in Figures 5 and 6; see Table S3 in the Supporting Information for important bond distances and angles. In both complexes, two sets of bis(1-pyrazolyl)methane units on two "arms" of the same ligand chelate a silver ion on the opposite sides of the ring, forming a double, mononuclear metallacyclic structure. In the metallacycle located on the left side of the arene rings in Figures 5 and 6, the arms (silver-colored bonds containing O(1) and O(4)) are oriented *para* on the central arene ring and chelate Ag(1) to form a 17-membered ring. The other metallacycle, located on the right side of the arene rings, forms a 16-membered ring by the chelation of a silver ion with bis(1-pyrazolyl)methane units of two arms oriented *meta* on the arene ring (red-colored bonds containing O(3) and O(5)). Again, the environments about the four-coordiante silver(I) cations can be described by τ_4, and these values are listed in Table 2. The values lie between 0.64 and 0.67, indicating that the silver environment is a distorted tetrahedral geometry. As observed in the silver complexes of $\mathbf{L_{tetra}}$, the silver−arene distances are too long to support any interactions between the cental arene ring and the silver cation with distances ranging from 4.12 to 4.82 Å.[16]

The remaining two arms of each $\mathbf{L_{hexa}}$ ligand, those not participating in the formation of a metallacycle (green bonds containing O(2) and O(6)) and oriented *meta* on the central arene ring, coordinate to two crystallographically equivalent silver ions linking the metallacycles into 1-D coordination polymers. Surprisingly, in both **3a** and **4a**, the silver cations, Ag(3), that link the double metallacylic unit into chains are not four-coordinate like Ag(1) and Ag(2); instead they are five-coordinate.

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(16) (a) Lindeman, S. V.; Rathore, R.; Kochi, J. K. *Inorg. Chem.* **2000**, *39*, 5707. (b) Munakata, M.; Wu, L. P.; Ning, G. L.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Maeno, N. *J. Am. Chem. Soc.* **1999**, *121*, 4968.

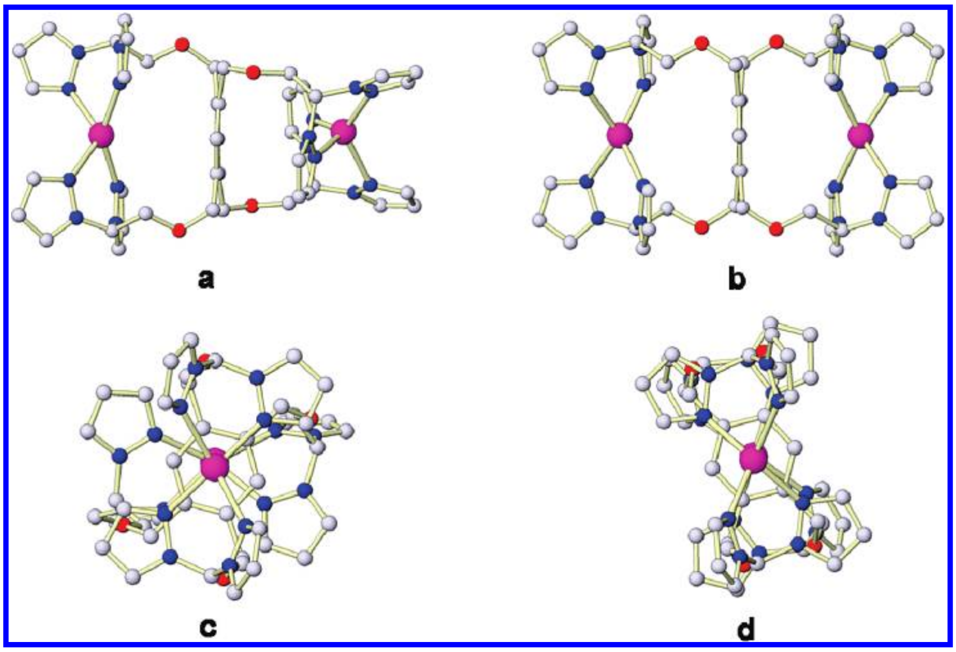

Figure 4. (a) Cation of **1a**. (b) Cation of **1b**. (c) Cation of **1a** viewed down the silver axis, perpendicular to the view in a. (d) Cation of **1b** viewed down the silver axis, perpendicular to the view in b.

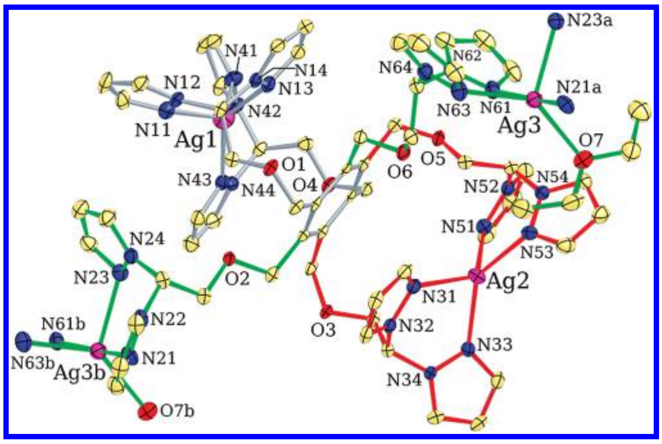

Figure 5. Structure of the cationic unit in $\{[Ag_3\mathbf{L_{hexa}}](BF_4)_3\cdot(C_4H_{10}O)\cdot5(CH_3CN)\}_n$ (**3a**). The *para*-linked metallacycle is indicated with silver bonds, the *meta*-linked metallacycle is indicated with red bonds, and the arms forming the coordination polymer are indicated with green bonds. Displacement parameters are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

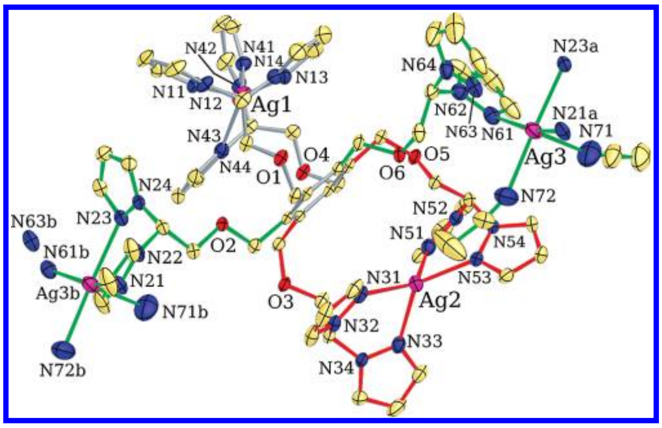

Figure 6. Structure of the cationic unit in $\{[Ag_3\mathbf{L_{hexa}}](ClO_4)_3\cdot2(CH_3CN)\cdot(solv)\}_n$ (**4a**). The *para*-linked metallacycle is indicated with silver bonds, the *meta*-linked metallacycle is indicated with red bonds, and the arms forming the coordination polymer are indicated with green bonds. Displacement parameters are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

The geometry of a five-coordinate system can be described using a parameter similar to τ_4. This parameter, τ_5, has been developed by Addison and Reedjik[17] to describe the geometry of a five-coordinate metal system, where

$$\tau_5 = \frac{(\beta - \alpha)}{60°}$$

and α and β are the two largest angles. A perfect square pyramid is given by a τ_5 value of 0, and a perfect trigonal bipyramid has a value of 1.

Although Ag(3) links $\mathbf{L_{hexa}}$ in both **3a** and **4a**, the ligands and the geometry around the metal are different in each structure. In the case of Ag(3) in **3a**, τ_5 is 0.52, indicating a highly distorted trigonal-bipyramidal configuration, Figure 5. The Ag(3) is bonded to two nitrogen atoms from one bis(1-pyrazolyl)methane unit oriented so that N(61) is in the axial position and N(63) is in an equatorial position. A second bis(1-pyrazolyl)methane unit from another $\mathbf{L_{hexa}}$ ligand is oriented so that N(21a) is in the axial position and N(23a) is in the equatorial position. The third equatorial position is filled with O(7) from the ether ligand. The nitrogen−silver bond distances range from 2.23 to 2.46 Å, and the silver−oxygen distance is 2.48 Å.

The Ag(3) in **4a** is also five-coordinate, but the arrangement is much closer to a square-pyramidal geometry with a τ_5 value of 0.14, Figure 6. The base of the pyramid is formed by N(21a) and N(23a) from one bis(1-pyrazolyl)methane unit, N(61) from a second bis(1-pyrazolyl)methane unit that is in the unusual κ^1-bonding mode,

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[17] Addison, A. W.; Rao, T. N.; Reedijk, J.; Van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

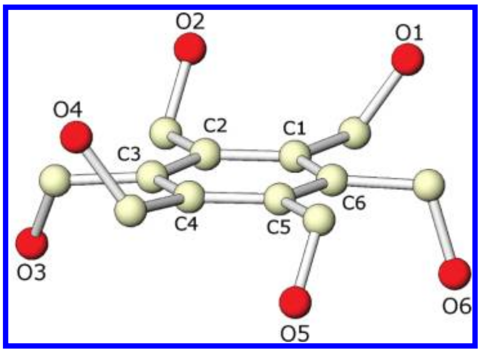

Figure 7. Drawing of the arene ring of $\mathbf{L_{hexa}}$ showing the orientation of the carbon and oxygen atoms of each arm in **3a** and **4a**.

and N(72) from a coordinated acetonitrile. Located at the apex of the pyramid is N(71) from a second coordinated acetonitrile. The bond lengths between silver and each nitrogen of the base range from 2.42 to 2.46 Å; however, the bond length of Ag(3)−N(71) is longer, with a distance of 2.63 Å. In the bis(1-pyrazolyl)methane unit that is κ^1-coordinated to Ag(3), the potential donor N(63) of the noncoordinated ring is positioned in proximity to Ag(3), but the N(63)···Ag(3) distance is too long at 2.731 Å to suggest anything other than a secondary interaction. Again, the chelate ring distorts the geometry around the silver with a N(21a)−Ag(3)−N(23a) angle of 81.8°.

Another unusual feature in both of the silver complexes containing $\mathbf{L_{hexa}}$ is the arrangement of the arms relative to the arene ring plane. To minimize steric interactions between neighboring groups on the ring, it is expected that the arms would be oriented in an alternating up−down arrangement.[18] However, as can be seen in Figure 7, the arms of $\mathbf{L_{hexa}}$ in **3a** and **4a**, beginning with the arm containing O(1) and moving counterclockwise, are arranged in an up, up, down, up, down, down orientation. This arrangement is controlled by the fact that one metallacyclic ring is formed by arms oriented *para* (O(1) and O(4)) and another metallacycle ring is formed by arms oriented *meta* (O(3) and O(5)); the oxygen atoms within a metallacycle must be on the same side of the ring, but each pair of oxygen atoms in each metallacycle must be on opposite sides of the ring.

Discussion

Given our previous work with ligands comprised of poly(1-pyrazolyl)methane units attached by flexible arms to a central arene core,[8,9,10e,11] the new silver(I) complexes of $\mathbf{L_{tetra}}$ could have had a variety of different structures: two *para*-linked or *meta*-linked metallacycles, one *para*-linked or *meta*-linked metallacycle connected into a coordination polymer, or a two-dimensional coordination polymer with no metallacycles. In fact, all five structures of the silver complexes of the tetratopic ligand $\mathbf{L_{tetra}}$ have a *double, mononuclear metallacyclic* motif, regardless of the counterion or solvents of crystallization. Two sets of *para*-oriented arms on the same ligand chelate two silver(I) ions, forming two mononuclear metallacycles, one on each side of the arene ring. The metallacyles formed are both 17-membered rings, like those formed in the silver complexes of $\mathbf{L_p}$. The metric parameters are similar in the silver complexes of both ligands, although the tetrahedral geometries around the silver ions in the double metallacyles are slightly more distorted, with τ_4 values averaging 0.58 and ranging from 0.51 to 0.72, compared to τ_4 values, which average 0.65 and range from 0.61 to 0.70 for $\mathbf{L_p}$ complexes. The flexibility of the ligand leads to two types of arrangements of the linking arms in the five complexes of $\mathbf{L_{tetra}}$.

For $\mathbf{L_{tetra}}$, the double metallacyclic motif can occur only with two *para*-linked or two *meta*-linked metallacycles, not one of each. Complexes of $\mathbf{L_{hexa}}$ remove this restriction so that two *para*-linked metallacycles, two *meta*-linked metallacycles, or one *para*-linked and one *meta*-linked metallacycle can form. The remaining two bis(pyrazolyl)methane units in $\mathbf{L_{hexa}}$ can be used only for the formation of a coordination polymer because once two metallacyclic rings form on each side of the arene ring, a third metallacycle cannot form due to sterics.

The result is that the silver(I) complexes of $\mathbf{L_{hexa}}$ also form double, mononuclear metallacycles, but the structures are different from those of the silver complexes of $\mathbf{L_{tetra}}$. The silver complexes of $\mathbf{L_{hexa}}$ contain both a *para*-linked and a *meta*-linked metallacycle. This result is surprising given that the structures of **1a**, **1b**, **2a**, and **2b** all form two *para*-linked metallacycles with tetratopic $\mathbf{L_{tetra}}$. As expected, the remaining two arms in the silver(I) complexes of $\mathbf{L_{hexa}}$ coordinate additional silver(I) cations, linking the double, mononuclear metallacycles into a coordination polymer network.

The reasons for the differing coordination preferences of $\mathbf{L_{tetra}}$ and $\mathbf{L_{hexa}}$ are not clear. The average τ_4 value for the $\mathbf{L_{hexa}}$ complexes is 0.66, which is higher than the 0.58 average observed for the $\mathbf{L_{tetra}}$ complexes, but not greatly different. The orientation of the arms relative to the plane of the arene ring for $\mathbf{L_{hexa}}$ does not seem to be a factor. In fact, the up, down, down, up, down, up orientation of the arms around the arene ring can be avoided only by the formation of two *meta*-linked metallacycles, the only configuration that we have not observed with either ligand. Apparently, both the 16- and 17-membered rings have about the same stability. The important point shown by these and our previous studies with $\mathbf{L_m}$ and $\mathbf{L_p}$ is that the *formation of 16- and 17-membered mononuclear metallacycles is strongly favored over coordination polymers* in these bis(pyrazolyl)methane-based systems.

Mononuclear rings of these sizes are unusual, with most mononuclear rings containing five or six atoms in the ring, and are simply considered coordination complexes. All of the complexes reported here contain these types of six-membered rings in addition to the larger rings. There are a few examples of larger mononuclear rings. Ward et al. have published an eight-membered ring formed by the chelation of silver from $AgNO_3$ by a 1,3-bis[3-pyridyl-1-pyrazolyl]propane ligand.[19] Stille has described a 12-membered ring where a 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene chelates a palladium.[20] Thompson et al. report that a larger 15-membered metallacycle is formed by an anionic hydrazone-based

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[19] Mann, K. L.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1998**, 3029.

[20] Gillie, A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4933.

ligand that links two tridentate groups that are chleated to a manganese cation in an octahedral environment.[21] These examples highlight the rarity of forming a large mononuclear metallacycle, and each case is a single mononuclear metallacycle. In this paper we report the first coordination complexes that form *double, mononuclear metallacyclic* structures from self-assembly. In a survey of the literature, no coordination compounds and only one example of a metal complex that could be considered a double, mononuclear metallacyclic was found. In this example, 1,1′-ferrocenedicarbaldehyde was condensed with a tetraamine-substituted arene to form two “18-membered” macrocycles.[22] Interestingly, in this case, the arene “arms” in both metallacycles are *meta*-oriented.

Importantly, none of the tris(1-pyrazolyl)methane ligand counterparts form structures analogous to those presented in this paper. The silver structures of the tetratopic and hexatopic ligands with tris(1-pyrazolyl)methane units coordinate silver cations in a κ^2-fashion, but form coordination polymers or cages,[8b,g,i] structures the $\mathbf{L_{tetra}}$ and $\mathbf{L_{hexa}}$ ligands could mimic but do not. The only structures formed by the bis(pyrazolyl)methane-based ligands that do not make metallacycles and do mimic their tris(1-pyrazolyl)methane counterpart contain the ditopic *ortho*-linked ligand, where both ligand types form coordination polymers. Presumably, in this case the metallacycle is not favored because of the strain that would be caused by utilizing adjacent arms on the linking arene ring.

The formation of coordination polymers with $\mathbf{L_{hexa}}$ using the two remaining arms not involved in the double metallacyle is expected. However, in both **3a** and **4a** the silver(I) cations (Ag(3)) involved in the polymer link are not four-coordinate, but instead are five-coordinate. Although examples of five-coordinate silver ions are known,[23] in our previous work with silver complexes of multitopic poly(pyrazolyl)methane ligands we have not encountered five-coordinate silver ions in coordination polymers. The bonding of the five-coordinate silver(I) in **4a** is very unusual in that one of the bis(1-pyrazolyl)methane units that forms the link in the coordination polymer is only κ^1-bonded, with two acetonitrile molecules from crystallization solvent filling out the coordination sphere in favor of forming the normal κ^2-chelate, six-membered ring. To the best of our knowledge, this complex is the first example of a bis(1-pyrazolyl)methane unit coordinating to silver in a κ^1-fashion.

Finally, as pointed out previously in the paper describing the chemistry of the $\mathbf{L_p}$ and $\mathbf{L_m}$ ligands, the single or double mononuclear metallacyclic structures do not favor extensive noncovalent interactions. In contrast, the coordination polymers formed by the tris(1-pyrazolyl)methane ligands and the *ortho*-substituted, bis(1-pyrazolyl)methane-based ligand $\mathbf{L_o}$ display much more complex supramolecular structures. Presumably the compact, basically spherical structures of the mononuclear metallacycles limit the orientations needed for extensive supramolecular interactions.

Conclusion

The new multitopic, bis(1-pyrazolyl)methane-based ligands 1,2,4,5-$C_6H_2[CH_2OCH_2CH(pz)_2]_4$ ($\mathbf{L_{tetra}}$) and $C_6[CH_2OCH_2CH(pz)_2]_6$ ($\mathbf{L_{hexa}}$) have been prepared. All of the silver(I) complexes of these ligands that have been studied adopt a new structural type from self-assembly: *double, mononuclear metallacycles*. The complexes of $\mathbf{L_{tetra}}$ form two *para*-linked mononuclear metallacycles, one on each side of the arene ring. The silver complexes of $\mathbf{L_{hexa}}$ also form double, mononuclear metallacycles, but in these cases one metallacycle is *para*-linked and the other is *meta*-linked. Clearly the formation of 16- and 17-membered mononuclear metallacycles is the favored arrangement for these polytopic ligands based on bis(pyrazolyl)methane units. The remaining two bis(pyrazolyl)methane units in $\mathbf{L_{hexa}}$ link the double metallacylic unit into a coordination polymer.

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Supporting Information Available: Full details of the refinement for each crystal structure, tables of bond distances and angles, and numbered structural diagrams of **1b** and **2a**. X-ray crystallographic files in CIF format. This information is available free of charge via the Internet at http://pubs.acs.org.

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