Inorg. Chem. **2009**, *48*, 936−945

Inorganic Chemistry
Article

# Mononuclear Metallacyclic Silver(I) Complexes of Third Generation Bis(1-pyrazolyl)methane Ligands

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Received August 21, 2008

The third-generation bis(1-pyrazolyl)methane ligands $p$-$C_6H_4[CH_2OCH_2CH(pz)_2]_2$ (**L$_p$**, pz = pyrazolyl ring) and $m$-$C_6H_4[CH_2OCH_2CH(pz)_2]_2$ (**L$_m$**) have been synthesized by the reaction of $(pz)_2CHCH_2OH$ with NaH followed by $\alpha,\alpha'$-dibromo-$p$-xylene or $\alpha,\alpha'$-dibromo-$m$-xylene. The reaction of **L$_p$** with $AgBF_4$, $AgPF_6$, and $AgO_3SCF_3$ yields the new compounds $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}BF_4$, $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}PF_6$, and $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}O_3SCF_3$, respectively. A similar reaction of **L$_m$** with $AgBF_4$ and $AgPF_6$ yields $\{Ag[m\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}BF_4$ and $\{Ag[m\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}PF_6$. These compounds were crystallized from both acetone and acetonitrile to yield nine crystalline forms of $(\mathbf{L}Ag)^+$ that differ in counterion and solvent of crystallization. In all complexes, the four pyrazolyl rings of the ligand chelate a single silver(I) cation in a distorted tetrahedral environment to form mononuclear metallacycles. This arrangement has not previously been observed with the analogous ligands based on tris(1-pyrazolyl)methane units and is unique because of the ring sizes (16-member rings in **L$_m$** and 17-member rings in **L$_p$**). The dominant feature in all of these solid state structures, regardless of solvent or anion, is this cationic metallacyclic architecture, which does not readily lend itself to strong supramolecular organization.

## Introduction

The covalent and supramolecular structures of self-assembled coordination networks composed of metal ions and multidentate organic ligands are of interest because the structures of materials govern properties, such as porosity,[1] magnetism,[2] and non-linear optical behavior.[3] One major challenge faced in designing materials with particular properties is controlling this coordination and self-assembly process, although systematic studies using a variety of ligands and metals have been carried out to probe these forces.[4] The results of these studies have demonstrated that control of ligand topicity, flexibility, or rigidity of the linker groups joining the coordination sites and the stereochemical preferences of the coordinated metal ion are all important in designing specific structures.[4] Non-covalent interactions are also important in organizing the coordination network and supramolecular structure. The most important forces impacting the supramolecular structures are strong[5] and weak[6] hydrogen bonds, $\pi$-$\pi$ stacking,[7] X—H···$\pi$ interactions (X = O, N, C),[8] and interhalogen interactions.[9] Many non-

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(5) Strong hydrogen bonds include interactions of the type O-H···O, N-H···O, O-H···N, and N-H···N. See for example. (a) Braga, D.; Grepioni, F. *J. Chem. Soc., Dalton Trans.* **1999**, 1. (b) Allen, M. T.; Burrows, A. D.; Mahon, M. F. *J. Chem. Soc., Dalton Trans.* **1999**, 215. (c) Ziener, U.; Breuning, E.; Lehn, J.-M.; Wegelius, E.; Rissanen, K.; Baum, G.; Fenske, D.; Vaughan, G. *Chem.—Eur. J.* **2000**, *6*, 4132. (d) Aakeröy, C. B.; Schultheiss, N.; Desper, J. *Inorg. Chem.* **2005**, *44*, 4983. (e) Burchell, T. J.; Eisler, D. J.; Puddephatt, R. J. *Inorg. Chem.* **2004**, *43*, 5550.

10.1021/ic801594q CCC: $40.75

**Chart 1.** $C_6H_{6\text{-}n}[CH_2OCH_2C(pz)_3]_n$ Family of Ligands

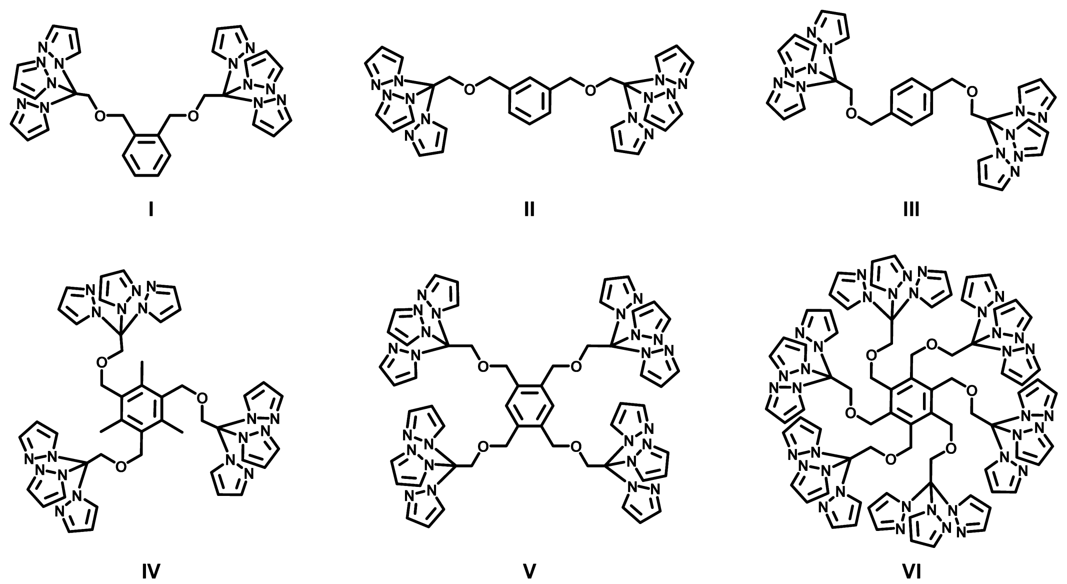
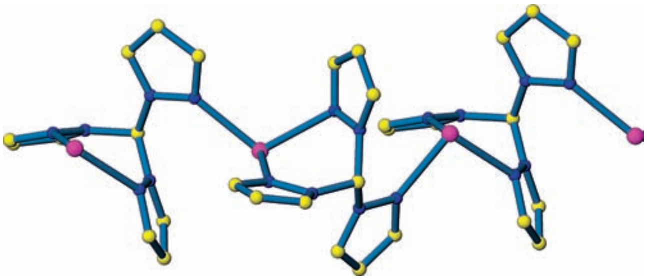


**Chart 2.** $\kappa^2$-$\kappa^1$ Coordination Mode of the [C(pz)$_3$] Units Linking the Silver Cations into Chains



covalent and covalent interactions involving the anions[10] and the solvents[11] were also found to have an impact on the crystal packing of a variety of compounds.

We have recently studied the silver(I) complexes of multitopic ligands built from tris(1-pyrazolyl)methane units of the general formula $C_6H_{6\text{-}n}[CH_2OCH_2C(pz)_3]_n$ ($n$ = 2, 3, 4, and 6, pz = pyrazolyl ring, Chart 1).[12] These "third generation" poly(pyrazolyl)methane ligands, ligands specifically functionalized at the non-coordinating "back" position, have been shown to be semi-rigid and ideal for studying the self-assembly process. Third generation ligands can be used to introduce functional groups that can enter into non-covalent interactions and also control the covalent bonding by altering the directional orientation of the poly(pyrazolyl)-methane units. Our most important and initially surprising result was that for cases where the metal is silver(I), the ligands usually display a $\kappa^2$-$\kappa^1$ coordination mode of the [C(pz)$_3$] units, which link the silver cations into chains, Chart 2.[12c,f−i] In addition, the "molecular" and supramolecular structures were dependent on the number of sidearms and ligand topology, that is, their position around the central arene ring, the solvent, and the counterion, with several different anions being involved in weak hydrogen bonds with the

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(6) Weak hydrogen bond (X-H$\cdots$Y) involves less electronegative atoms; we discuss here only C-H$\cdots$Y type of weak hydrogen bond (Y = O, F). See for example. (a) Favero, L. B.; Giuliano, B. M.; Melandri, S.; Maris, A.; Ottaviani, P.; Velino, B.; Caminati, W. *J. Phys. Chem. A* **2005**, *109*, 7402. (b) Calhorda, M. J. *Chem. Commun.* **2000**, 801. (c) Desiraju, G. R. *Acc. Chem. Res.* **1996**, *29*, 441. (d) D′Oria, E.; Novoa, J. J. *CrystEngComm* **2008**, *10*, 423.

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metal-organic-frameworks.[12b,c,f−i] While most silver(I) complexes display the $\kappa^2$-$\kappa^1$ coordination mode, for ligands where the sidearms are in close proximity, that is, in the ortho-linked, bitopic ligand and the 1,2,4,5-tetratopic ligand (I and V, Chart 1), the $\kappa^2$-$\kappa^0$ coordination mode was generally encountered.[12g]

To continue to systematically explore these ligand systems, we have prepared ligands that retain the features of the $C_6H_{6-n}[CH_2OCH_2C(pz)_3]_n$ series, but where the $\kappa^2$-$\kappa^1$ coordination mode of the tris(1-pyrazolyl)methane units is prevented by synthesizing analogous ligands based on bis(1-pyrazolyl)methane donor sets. In our first publication with these ligands, we have reported that in the case of a bitopic ligand with adjacent sidearms, *o*-$C_6H_4[CH_2OCH_2CH(pz)_2]_2$, the silver complexes form coordination polymers similar to the structures observed with *o*-$C_6H_4[CH_2OCH_2C(pz)_3]_2$.[13] Reported here are the syntheses and silver(I) chemistry of bitopic ligands containing bis(1-pyrazolyl)methane donor sets where the arms are not in close proximity, that is, *m*-$C_6H_4[CH_2OCH_2CH(pz)_2]_2$ and *p*-$C_6H_4[CH_2OCH_2CH(pz)_2]_2$. The structures of these new complexes are all unusual mononuclear metallacycles that are very different from previously reported complexes of the ortho-linked bis(pyrazolyl)methane ligand or the analogous ligands with tris(pyrazolyl)methane donor sets.

## Experimental Section

**General Procedure.** All operations were carried out under a nitrogen atmosphere using standard Schlenk techniques and a Vacuum Atmospheres HE-493 dry box. The tetrahydrofuran was dried and distilled prior to use following standard techniques. Other solvents were used as received. The $^1$H NMR spectra were recorded on a Varian AM300 spectrometer using a broadband probe. Proton chemical shifts are reported in ppm and were referenced to undeuterated solvent signals ($^1$H) or deuterated solvent signals ($^{13}$C). Elemental analyses were performed by Robertson Microlit Laboratories (Madison, NJ). The 2,2′-bis(1-pyrazolyl)ethanol was prepared following the published method.[13] Silver tetrafluoroborate, silver hexafluorophosphate, silver trifluoromethanesulfonate, α,α′-dibromo-*p*-xylene, and α,α′-dibromo-*m*-xylene were obtained from commercial sources (Aldrich) and used as received.

**Synthesis of *p*-$C_6H_4[CH_2OCH_2CH(pz)_2]_2$ ($L_p$).** In a three-necked 500 mL flask, fitted with a condenser and a vacuum adapter, NaH (0.314 g, 13.1 mmol) was suspended in 200 mL tetrahydrofuran (THF), and 2,2′-bis(1-pyrazolyl)ethanol (2.332 g, 13.1 mmol) was added against a stream of nitrogen. Gas evolution was noted. The reaction was heated at reflux for 45 min, during which time the mixture turned yellow and became less cloudy. After 45 min a solution of α,α′-dibromo-*p*-xylene (1.73 g, 6.54 mmol) in 50 mL of THF was added dropwise to the refluxing solution over a span of 80 min. The reaction was then heated for 72 h at reflux, during which time a white precipitate formed. The mixture was cooled to room temperature, and 100 mL of water was added to dissolve the precipitate. The solution was extracted with dichloromethane (4 × 100 mL). The combined organic layer was dried with $MgSO_4$ and filtered. The solvent was removed in vacuo to give an off-white solid. The solid was dissolved in 40 mL of hot ethanol, and the volume was reduced to 15 mL. The solution was cooled and crystals formed. The liquid was decanted off, and the remaining crystals were washed with cold ethanol. The crystals were dried under high vacuum to afford the desired product. Yield: 1.783 g (59%). Mp 119−122 °C. Anal. Calcd for $C_{24}H_{26}N_8O_2$: C, 62.87; H, 5.72; N, 24.44. Found: C, 62.59; H, 5.60; N, 24.10. $^1$H NMR (acetonitrile-d$_3$): $\delta$ 7.76, 7.49 (d, d, $J = 1.8$ Hz, $J = 1.8.$ Hz, 4 H, 4 H, 3,5-H-pz), 7.18 (s, 4 H, $C_6H_4$), 6.66 (t, $J = 6.6$ Hz, 2 H, CH(pz)$_2$), 6.30 (t, $J = 2.1$ Hz, 4 H, 4-H-pz), 4.52 (s, 4 H, ArCH$_2$), 4.39 (d, $J = 7.2$ Hz, 4 H, OCH$_2$CH). $^{13}$C NMR (acetonitrile-d$_3$): $\delta$ 140.9 (pz), 138.4 (arene), 130.2 (arene), 128.8 (pz), 107.1 (pz), 74.6, 73.6, 70.0. MS ESI(+) *m/z* (rel. % abund.) [assgn]: 481 (27) $[\mathbf{L_p}+Na]^+$, 459 (100) $[\mathbf{L_p}+H]^+$, 391 (5) $[\mathbf{L_p}-pz]^+$.

**Synthesis of *m*-$C_6H_4[CH_2OCH_2CH(pz)_2]_2$ ($L_m$).** In a 250 mL round-bottom Schlenk flask, NaH (0.157 g, 6.54 mmol) was suspended in 125 mL of THF. 2,2′-Bis(1-pyrazolyl)ethanol (1.166 g, 6.54 mmol) was added against a stream of nitrogen, and gas evolution was noted. After 90 min, NaI (0.654 g, 4.36 mmol) and α,α′-dibromo-*m*-xylene (0.576 g, 2.18 mmol) were added to the mixture. The reaction mixture was heated at reflux for 13 days. The reaction was cooled, and 100 mL of water was added to give a clear yellow solution. This solution was extracted with 100 mL of dichloromethane three times. The combined organic layer was washed with 100 mL of saturated sodium thiosulfate solution. The organic layer was then dried with $MgSO_4$ and filtered. The solvent was removed in vacuo to give an oil. The product was purified by chromography on a silica gel column using 1:1 ethyl acetate:hexanes as eluent. The product was isolated as a cloudy viscous oil. Yield: 0.571 g (57%). $^1$H NMR (acetonitrile-d$_3$): $\delta$ 7.75, 7.49 (d, d, $J = 2.7$ Hz, $J = 1.5$ Hz, 4 H, 4 H, 3,5-*H*-pz), 7.31−7.07 (m, 4 H, C$_6$*H*$_4$), 6.66 (t, $J = 6.9$ Hz, 2 H, C*H*(pz)$_2$), 6.28 (t, $J = 2.1$ Hz, 4 H, 4-*H*-pz), 4.51 (s, 4 H, ArC*H*$_2$), 4.40 (d, $J = 6.9$ Hz, 4 H, OC*H*$_2$CH). $^{13}$C NMR (acetonitrile-d$_3$): $\delta$ 140.9 (pz), 139.0 (arene), 130.2 (arene), 129.4, 128.2, 128.1, 107.2 (arene + pz), 74.6, 73.7, 70.1. MS ESI(+) *m/z* (rel. % abund.) [assgn]: 481 (32) $[\mathbf{L_m}+Na]^+$, 459 (100) $[\mathbf{L_m}+H]^+$, 391 (7) $[\mathbf{L_m}\text{-pz}]^+$. HRMS: ES$^+$ (*m/z*): $[\mathbf{L_m}+H]^+$ calcd for $[C_{24}H_{27}N_8O_2]^+$ 459.2257; found 459.2275.

**Synthesis of $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}BF_4$ (1).** $\mathbf{L_p}$ (0.229 g, 0.50 mmol) was added to a 100 mL Schlenk flask containing 50 mL of THF followed by the addition of $AgBF_4$ (0.097 g, 0.50 mmol) against a stream of nitrogen. The reaction was stirred for 24 h, during which time a white precipitate formed. The system was cannula filtered, and the solid washed with 5 mL of THF. The white solid was dried at 65 °C in vacuo. Yield: 0.170 g (52%). $^1$H NMR (acetonitrile-d$_3$): $\delta$ 7.90, 7.50 (d, d, $J = 2.4$ Hz, $J = 2.1$ Hz, 4 H, 4 H, 3,5-*H*-pz), 6.95 (s, 4 H, arene), 6.70 (t, $J = 7.2$ Hz, 2 H, C*H*(pz)$_2$), 6.38 (t, $J = 2.1$ Hz, 4 H, 4-*H*-pz), 4.49 (s, 4 H, ArC*H*$_2$), 4.31 (d, $J = 7.2$ Hz, 4 H, OC*H*$_2$CH). $^{13}$C NMR (acetonitrile-d$_3$): $\delta$ 143.3 (pz), 137.8 (arene), 133.2 (arene), 130.1 (pz), 107.3 (pz), 73.6, 72.6, 67.1. MS ESI(+) *m/z* (rel. % abund.) [assgn]: 565 (100) $[\mathbf{L_p}Ag]^+$, 481 (54) $[\mathbf{L_p}+Na]^+$, 459 (73) $[\mathbf{L_p}+H]^+$. HRMS: ES$^+$ (*m/z*): $[\mathbf{L_p}Ag]^+$ calcd for $[C_{24}H_{26}N_8O_2Ag]^+$ 565.1230; found 565.1233.

**Synthesis of $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}PF_6$ (2).** This compound was prepared as **1** using $\mathbf{L_p}$ (0.229 g, 0.50 mmol) and $AgPF_6$ (0.126 g, 0.50 mmol). Yield: 0.138 g (39%). Anal. Calcd for $C_{24}H_{26}N_8O_2AgPF_6$: C, 40.52; H, 3.68; N, 15.75. Found: C, 40.56; H, 3.30; N, 15.44. $^1$H NMR (acetonitrile-d$_3$): $\delta$ 7.88, 7.50 (d, d, $J = 1.8$ Hz, $J = 2.1.$ Hz, 4 H, 4 H, 3,5-*H*-pz), 6.97 (s, 4 H, C$_6$*H*$_4$), 6.69 (t, $J = 7.2$ Hz, 2 H, C*H*(pz)$_2$), 6.37 (t, $J = 2.4$ Hz, 4 H, 4-*H*-pz), 4.49 (s, 4 H, ArC*H*$_2$), 4.31 (d, $J = 7.2$ Hz, 4 H, OC*H*$_2$CH). $^{13}$C NMR (acetonitrile-d$_3$): $\delta$ 143.1 (pz), 137.9 (arene), 133.0 (arene), 130.0 (pz), 107.2 (pz), 73.6, 72.7, 67.3. MS ESI(+) *m/z* (rel. % abund.) [assgn]: 565 (100) $[\mathbf{L_p}Ag]^+$, 481 (12) $[\mathbf{L_p}+Na]^+$, 459 (73) $[\mathbf{L_p}+H]^+$.

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**Table 1.** Selected Crystal Data and Structure Refinement for **1a**, **1b**, **1c**, **2b**, and **3a**

| | **1a** | **1b** | **1c** | **2b** | **3a** |
|---|---|---|---|---|---|
| formula | $C_{25.50}H_{29}AgBF_4N_8O_{2.50}$ | $C_{24}H_{26}AgBF_4N_8O_2$ | $C_{24}H_{26}AgBF_4N_8O_2$ | $C_{26}H_{29}AgF_6N_9O_2P$ | $C_{28}H_{32}AgF_3N_8O_6S$ |
| fw, g $mol^{-1}$ | 682.25 | 653.21 | 653.21 | 752.42 | 773.55 |
| cryst syst | triclinic | triclinic | triclinic | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $T$, K | 150(1) | 150(1) | 150(1) | 150(1) | 150(1) |
| $a$, Å | 8.7903(3) | 8.3975(3) | 8.3522(5) | 8.7153(3) | 8.3402(4) |
| $b$, Å | 12.6297(4) | 12.4049(4) | 12.5650(7) | 12.0822(4) | 13.8165(6) |
| $c$, Å | 26.7071(9) | 26.3225(9) | 13.5265(7) | 15.5978(5) | 14.9042(7) |
| α, deg | 101.437(1) | 87.462(1) | 83.290 (1) | 77.674 (1) | 102.621 (1) |
| $\beta$, deg | 94.093(1) | 86.517(1) | 78.413 (1) | 75.504 (1) | 90.540 (1) |
| $\gamma$, deg | 97.523(1) | 78.450(1) | 70.641 (1) | 75.623 (1) | 98.945 (1) |
| $V$, Å$^3$ | 2866.61(16) | 2680.09(16) | 1310.05(13) | 1520.18(9) | 1653.89(13) |
| $Z$ | 4 | 4 | 2 | 2 | 2 |
| R1 ($I > 2\sigma(I)$) | 0.0422 | 0.0439 | 0.0253 | 0.0301 | 0.0376 |
| wR2 ($I > 2\sigma(I)$) | 0.0984 | 0.0943 | 0.0652 | 0.0738 | 0.1005 |

**Synthesis of $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}O_3SCF_3$ (3).** This compound was prepared as **1** using $\mathbf{L_p}$ (0.229 g, 0.50 mmol) and $AgO_3SCF_3$ (0.128 g, 0.50 mmol). Yield: 0.241 g (68%). Anal. Calcd for $C_{25}H_{26}N_8O_5AgF_3S$: C, 41.96; H, 3.66; N, 15.67. Found: C, 42.25; H, 3.82; N, 15.36. $^1$H NMR (acetonitrile-d$_3$): $\delta$ 7.88, 7.50 (d, d, $J$ = 2.4 Hz, $J$ = 2.1. Hz, 4 H, 4 H, 3,5-*H*-pz), 6.97 (s, 4 H, $C_6H_4$), 6.69 (t, $J$ = 7.2 Hz, 2 H, C*H*(pz)$_2$), 6.37 (t, $J$ = 2.1 Hz, 4 H, 4-*H*-pz), 4.50 (s, 4 H, ArC*H*$_2$), 4.31 (d, $J$ = 6.9 Hz, 4 H, OC*H*$_2$CH). $^{13}$C NMR (acetonitrile-d$_3$): $\delta$ 143.1 (pz), 137.9 (arene), 132.9 (arene), 130.0 (pz), 107.2 (pz), 73.6, 72.7, 67.4. MS ESI(+) *m*/*z* (rel. % abund.) [assgn]: 565 (100) [$\mathbf{L_p}$Ag]$^+$, 481 (39) [$\mathbf{L_p}$+Na]$^+$, 459 (91) [$\mathbf{L_p}$+H]$^+$.

**Synthesis of $\{Ag[m\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}BF_4$ (4).** In a 100 mL Schlenk flask, the ligand, $\mathbf{L_m}$, (0.229 g, 0.50 mmol) was dissolved in 25 mL of THF. The $AgBF_4$ (0.097 g, 0.50 mmol) was added to the solution against a stream of nitrogen. A white precipitate formed immediately. The reaction was stirred for 19 h. The system was then cannula filtered to give a white solid, which was washed with 5 mL of THF. The white solid was dried in vacuo. Yield 0.263 g (80%). Anal. Calcd for $C_{24}H_{26}N_8O_2AgBF_4$: C, 44.13; H, 4.01; N, 17.15. Found: C, 44.05; H, 3.81; N, 16.77. $^1$H NMR (acetonitrile-d$_3$): $\delta$ 7.89, 7.52 (d, d, $J$ = 2.4 Hz, $J$ = 1.8 Hz, 4 H, 4 H, 3,5-*H*-pz), 7.18–6.92 (2nd order m, 4 H, $C_6H_4$), 6.72 (t, $J$ = 6.9 Hz, 2 H, C*H*(pz)$_2$), 6.36 (t, $J$ = 2.1 Hz, 4 H, 4-*H*-pz), 4.47 (d, $J$ = 5.7 Hz, 4 H, OC*H*$_2$CH), 4.46 (s, 4 H, ArC*H*$_2$). $^{13}$C NMR (acetonitrile-d$_3$): $\delta$ 143.3 (pz), 138.2 (arene), 133.1 (arene), 129.9, 129.0, 128.7, 107.4 (arene + pz), 73.9, 73.3, 68.6. MS ESI(+) *m*/*z* (rel. % abund.) [assgn]: 565 (100) [$\mathbf{L_m}$Ag]$^+$, 481 (51) [$\mathbf{L_m}$+Na]$^+$, 459 (88) [$\mathbf{L_m}$+H]$^+$.

**Synthesis of $\{Ag[m\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}PF_6$ (5).** In a 100 mL Schlenk flask, the ligand, $\mathbf{L_m}$, (0.229 g, 0.50 mmol) was dissolved in 25 mL of THF. The $AgPF_6$ (0.126 g, 0.50 mmol) was added to the solution against a stream of nitrogen. The reaction was stirred for 18 h, and a pale purple solid was noted. The system was cannula filtered, and the solid washed with 5 mL of THF. The solvent from the filtering and the washing was combined, and 25 mL of ether was added. A white precipitate formed. The system was cannula filtered again to give a white solid. The solid was washed with 5 mL of ether. The solid was dried at 65 °C to afford the desired product. Yield 0.213 g (60%). Anal. Calcd for $C_{24}H_{26}N_8O_2AgPF_6$: C, 40.52; H, 3.68; N, 15.75. Found: C, 40.90; H, 3.86; N, 15.38. $^1$H NMR (acetonitrile-d$_3$): $\delta$ 7.89, 7.53 (d, d, $J$ = 2.4 Hz, $J$ = 1.8 Hz, 4 H, 4 H, 3,5-*H*-pz), 7.18–6.91 (2nd order m, 4 H, $C_6H_4$), 6.72 (t, $J$ = 6.9 Hz, 2 H, C*H*(pz)$_2$), 6.37 (t, $J$ = 2.1 Hz, 4 H, 4-*H*-pz), 4.47 (d, $J$ = 5.7 Hz, 4 H, OC*H*$_2$CH), 4.46 (s, 4 H, ArC*H*$_2$). $^{13}$C NMR (acetonitrile-d$_3$): $\delta$ 143.2 (pz), 138.2 (arene), 132.9 (arene), 129.9, 128.9, 128.7, 107.4 (arene + pz), 73.9, 73.3, 68.7. MS ESI(+) *m*/*z* (rel. % abund.) [assgn]: 565 (100) [$\mathbf{L_m}$Ag]$^+$, 481 (35) [$\mathbf{L_m}$+Na]$^+$, 459 (74) [$\mathbf{L_m}$+H]$^+$. HRMS: ES$^+$ (*m*/*z*): [$\mathbf{L_m}$Ag]$^+$ calcd for $[C_{24}H_{26}N_8O_2Ag]^+$ 565.1230; found 565.1232.

**Crystallography.** X-ray diffraction intensity data for each compound were measured at 150(1) K on a Bruker SMART APEX diffractometer (Mo Kα radiation, $\lambda$ = 0.71073 Å).[14] Raw area detector data frame integration was performed with SAINT+.[14] Final unit cell parameters were determined by least-squares refinement of strong reflections from the data set (9899 for **1a**, 6845 for **1b**, 6202 for **1c**, 8201 for **2b**, 6397 for **3a**, 6840 for **3b**, 9451 for **4b**, 5481 for **5a**, and 7740 for **5b**). All compounds crystallize in the triclinic crystal system. The space group $P\bar{1}$ was confirmed for each by the successful solution and refinement of the structures. Direct methods solution, difference Fourier calculations and full-matrix least-squares refinement against $F^2$ were performed with SHELXTL.[15] All non-hydrogen atoms were refined with anisotropic displacement parameters except where noted (**1a**, **1b**, and **3a**). Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms. Information regarding the structure solution and refinement for each structure is given below, and the numerical results are given in Tables 1 and 2.

**General Crystallization Procedures.** All crystals were grown by the method of vapor phase diffusion. Approximately 10 mg of the appropriate powder was dissolved in 1 mL of acetone or acetonitrile. This solution was placed into a small test tube, which was then placed into a larger test tube containing diethyl ether and sealed. Crystals grew within 1 to 14 days.

Compound **1a**, $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}BF_4 \cdot 0.5\text{-}((CH_3)_2CO)$, crystallizes with two independent $[Ag(C_{24}H_{26}N_8O_2)]^+$ cations, two independent $BF_4^-$ anions, and one acetone molecule of crystallization in the asymmetric unit. The $BF_4^-$ anion B2 is disordered and was modeled as occupying two closely separated positions in the refined fractions B2A/B2B = 0.708(6)/0.292(6). The geometry of both disorder components was restrained to be similar to that of the ordered anion B1 (Shelx SAME instruction, 30 restraints).

Compound **1b**, $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}BF_4$, crystallizes with two crystallographically independent $Ag(C_{24}H_{26}N_8O_2)^+$ cations and two independent $BF_4^-$ counterions in the asymmetric unit. One of the $BF_4^-$ ions (B2/F5–F8) is disordered and was modeled as occupying three distinct but closely separated positions (A/B/C), in the refined populations A/B/C = 0.48(1)/0.39(1)/0.13(1). The geometry of each disorder component was restrained to be similar to that of the ordered $BF_4^-$ ion (B1/F1–F4, 61 restraints), and all constituent atoms were refined isotropically.

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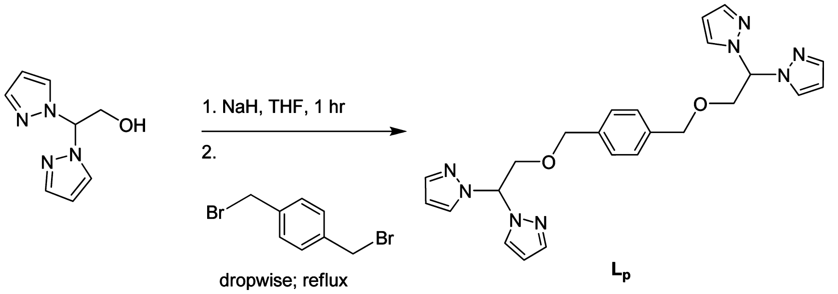
[14] *SMART, version 5.625, SAINT+, version 6.45*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2001.

[15] *SHELXTL, version 6.14*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 2000.

**Table 2.** Selected Crystal Data and Structure Refinement for **3b**, **4b**, **5a**, and **5b**

| | **3b** | **4b** | **5a** | **5b** |
|---|---|---|---|---|
| formula | $C_{26}H_{27.50}AgF_3N_{8.50}O_5S$ | $C_{24}H_{26}AgBF_4N_8O_2$ | $C_{27}\ H_{32}AgF_6N_8O_3P$ | $C_{25}H_{27.50}AgF_6N_{8.50}O_2P$ |
| fw, g mol$^{-1}$ | 735.99 | 653.21 | 769.45 | 731.89 |
| cryst syst | triclinic | triclinic | triclinic | triclinic |
| space group | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ | $P\bar{1}$ |
| $T$, K | 150(1) | 150(1) | 150(1) | 150(1) |
| $a$, Å | 8.2789(3) | 8.4029(5) | 8.3160(4) | 8.3095(6) |
| $b$, Å | 18.5091(8) | 17.5838(11) | 15.9400(8) | 18.4719(14) |
| $c$, Å | 20.3995(9) | 18.3807(12) | 24.3866(12) | 19.4738(15) |
| $\alpha$, deg | 86.069(1) | 88.116(1) | 78.185(1) | 82.317(0) |
| $\beta$, deg | 79.430(1) | 83.671(1) | 85.558(1) | 89.550(1) |
| $\gamma$, deg | 82.577(1) | 82.732(1) | 83.090(1) | 80.910(1) |
| $V$, Å$^3$ | 3043.9(2) | 2677.1(3) | 3136.5(3) | 2924.8(4) |
| $Z$ | 4 | 4 | 4 | 4 |
| R1 ($I > 2\sigma(I)$) | 0.0412 | 0.0382 | 0.0504 | 0.0401 |
| wR2 ($I > 2\sigma(I)$) | 0.0720 | 0.1012 | 0.1075 | 0.0977 |

**Scheme 1.** Synthesis of $\mathbf{L_p}$



Compound **1c**, $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}BF_4$, crystallizes with one $Ag(C_{24}H_{26}N_8O_2)^+$ cation and one $BF_4^-$ anion in the asymmetric unit.

Compound **2b**, $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}PF_6\cdot(CH_3CN)$, crystallizes with one $Ag(C_{24}H_{26}N_8O_2)^+$ cation, one $PF_6^-$ anion and one acetonitrile molecule of crystallization in the asymmetric unit.

Compound **3a**, $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}SO_3CF_3\cdot((CH_3)_2CO)$, crystallizes with one $Ag(C_{24}H_{26}N_8O_2)^+$ cation, one triflate anion, and one acetone molecule of crystallization in the asymmetric unit. The triflate anion is disordered over two orientations on the refined ratio 0.861(3)/0.139(3). The geometry of the minor disorder component was restrained to be similar to that of the major component (SHELX SAME instruction, 19 total restraints). Atoms of the minor disorder component were refined with a common isotropic displacement parameter.

Compound **3b**, $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}SO_3CF_3\cdot 0.5(CH_3CN)$, crystallizes with two independent $Ag(C_{24}H_{26}N_8O_2)^+$ cations, two independent triflate counterions, and one acetonitrile molecule of crystallization in the asymmetric unit.

Compound **4b**, $\{Ag[m\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}BF_4$, crystallizes with two independent $Ag(C_{24}H_{26}N_8O_2)^+$ cations and two independent $BF_4^-$ anions in the asymmetric unit. The ligand bonded to Ag2 is disordered and was modeled as occupying two different positions which are similar in conformation. The disorder primarily affects the middle -$(CH_2OCH_2)_2C_6H_4$ section of the ligand (atoms labeled C101−C110, O3A/O4A and C201−C210, O3B/O4B). The -$C(pz)_2$ ends of the ligand are also affected by the disorder but to a lesser degree and were modeled with only one average component. This is the reason for the slightly irregular geometry around the central carbon atom of this ligand. The phenyl rings of the disordered ligand were modeled as rigid hexagons of variable size; matching bonds between the disorder components were restrained to have similar distances (SHELX SADI instruction, 12 restraints).

Compound **5a**, $\{Ag[m\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}PF_6\cdot((CH_3)_2CO)$, crystallizes with two independent $Ag(C_{24}H_{26}N_8O_2)^+$ cations, two $PF_6^-$ anions, and two acetone molecules of crystallization in the asymmetric unit.

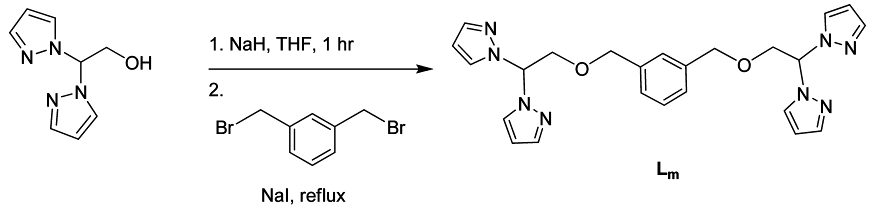
Compound **5b**, $\{Ag[m\text{-}C_6H_4(CH_2OCH_2CH(pz)_2)_2]\}PF_6\cdot 0.5(CH_3CN)$, crystallizes with two independent $Ag(C_{24}H_{26}N_8O_2)^+$ cations, two $PF_6^-$ anions, and one acetonitrile molecule of crystallization in the asymmetric unit.

## Results

**Synthesis and Characterization.** The synthesis of $p\text{-}C_6H_4[CH_2OCH_2CH(pz)_2]_2$, $\mathbf{L_p}$, is shown in Scheme 1. The 2,2-bis(1-pyrazolyl)ethanol was added to a suspension of sodium hydride to form the alkoxide in situ. To this mixture heating at reflux, α,α′-dibromo-*p*-xylene was added dropwise to give the desired ligand $\mathbf{L_p}$. If the α,α′-dibromo-*p*-xylene is added all at once to the alkoxide mixture, a side reaction occurs in which an insoluble, bright yellow solid forms.

The synthesis of $m\text{-}C_6H_4[CH_2OCH_2CH(pz)_2]_2$, $\mathbf{L_m}$, was attempted by mixing the alkoxide, formed in situ from the stoichiometric reaction of sodium hydride with 2,2-bis(pyrazolyl)ethanol, and α,α′-dibromo-*m*-xylene. The yield from this method was low with substantial starting material and the intermediate α-bromo-,α′-bis(1-pyrazolyl)ethyl ether-*m*-xylene also present. Isolating the pure ligand $\mathbf{L_m}$ from this reaction mixture was difficult. To avoid these problems, an excess of the bis(1-pyrazolyl)ethoxide was added, as well as sodium iodide. The sodium iodide presumably displaces the bromine in the α,α′-dibromo-*m*-xylene, giving the electrophilic site a better leaving group, which in turn promotes the desired nucleophilic substitution reaction with

**Scheme 2.** Synthesis of $\mathbf{L_m}$



the alkoxide.[16] The sodium iodide can be added in catalytic amounts, but the reaction was completed sooner when stoichiometric amounts of sodium iodide were used. Scheme 2 shows the best conditions found to synthesize the pure ligand $\mathbf{L_m}$.

The preparations of **1**−**3** were readily achieved by combining equal molar amounts of $\mathbf{L_p}$ with $AgBF_4$, $AgPF_6$, or $AgO_3SCF_3$ to give {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$BF_4$ (**1**), {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$PF_6$ (**2**), and {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$O_3SCF_3$ (**3**). The preparations of **4** and **5** were achieved by combining equal molar amounds of $\mathbf{L_m}$ with $AgBF_4$ or $AgPF_6$ to give {Ag[*m*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$BF_4$ (**4**) and {Ag[*m*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$PF_6$ (**5**). These compounds are white solids that are air-stable and show only slight decomposition after several weeks of exposure to daylight. The same compounds **1**−**3** also form in reactions that contain 1 equiv of $\mathbf{L_p}$ and 2 equiv of $AgBF_4$, $AgPF_6$, or $AgO_3SCF_3$, respectively. The complex made from $\mathbf{L_m}$ and $AgO_3SCF_3$ did not produce crystals suitable for X-ray crystallography studies and was not studied farther.

The $^1H$ NMR spectra of the all silver(I) complexes 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). In our previous studies of silver(I) complexes of tris(1-pyrazolyl)methane ligands, acetonitrile does displace the tris(1-pyrazolyl)methane units.[12g,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**, **2**, and **3** are essentially identical, as are the spectra of **4** and **5**. This result suggests that the cationic species present in solution are anion independent. Electrospray mass spectroscopy of **1**−**5** shows peaks corresponding to the cationic unit, $[\mathbf{L}Ag]^+$, as well as $[\mathbf{L}+H]^+$ and $[\mathbf{L}+Na]^+$.

**Formation of Single Crystals.** Crystals of {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$BF_4\cdot 0.5((CH_3)_2CO)$ (**1a**), {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$SO_3CF_3\cdot((CH_3)_2CO)$ (**3a**), and {Ag[*m*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$PF_6\cdot((CH_3)_2CO)$ (**5a**) were grown by vapor diffusion of diethyl either into acetone solutions of compounds **1**, **3**, and **5**, respectively. Crystals of {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$BF_4$ (**1b**), {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$PF_6\cdot(CH_3CN)$ (**2b**), {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$SO_3CF_3\cdot 0.5(CH_3CN)$ (**3b**), {Ag[*m*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$BF_4$ (**4b**), and {Ag[*m*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$PF_6\cdot 0.5(CH_3CN)$ (**5b**) were grown by vapor diffusion of diethyl ether into acetonitrile solutions of compounds **1**, **2**, **3**, **4**, and **5**, respectively. Compound **1** and **3** formed in a reaction with 2 equiv of $AgBF_4$ crystallized from acetone to give **1a** and **3a**, respectively. However, when **1** made in this manner was crystallized from acetonitrile a polymorph of **1b**, {Ag[*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$]}$BF_4$ (**1c**), formed. Significant bond lengths and angles are listed in Table 3.

**Crystal Structures of Complexes of [*p*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$].** The structures of the cationic unit in all the silver complexes containing $\mathbf{L_p}$ are very similar mononuclear metallacycles despite differences in the crystal structures because of solvent molecules or different counterions present. Three of the silver compounds, **1c**, **2b**, and **3a**, contain one crystallographically independent cationic unit (Figure 1 shows **1c**; **2b** and **3a** same numbering), whereas compounds **1a**, **1b**, and **3b** have two crystallographically independent cationic units (Figure 2 shows **1a**; **1b** and **3b** same numbering). In all of these compounds, the ligand is tetradentate and bonds a single silver cation, which gives rise to the 17-member metallacyclic structures seen in Figures 1 and 2. The four pyrazolyl rings from the ligands chelate the silver atoms in a distorted-tetrahedral environment. The main distortion is caused by the restricted "bite" angle of each bis(1-pyrazolyl)methane unit that lowers the corresponding N−Ag−N angles, ranging from 82.6° to 85.8° (for a complete list see Table 3). The nitrogen−silver bond lengths are within the normal range for these types of compounds[12h,13,17] (see Table 3), although the variations within any given structure can be over 0.2 Å. The Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawings seem to show that the linking arene ring of the ligand is in proximity to the silver, but the silver−central arene ring distances range from 3.93Å to 4.23Å, indicating that no silver−arene ring interactions are present in any of the structures.[18]

**Crystal Structures of Complexes of [*m*-$C_6H_4(CH_2OCH_2CH(pz)_2)_2$].** The structures of all the cationic units of silver complexes containing $\mathbf{L_m}$ are mononuclear metallacycles similar to those formed with $\mathbf{L_p}$. Figure 3 shows the two independent cationic units for **5a**, same numbering scheme applies to **4b** and **5b**, which also have two independent cationic units. As observed with $\mathbf{L_p}$, in all cases $\mathbf{L_m}$ is a

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**Table 3.** Selected Bond Distances (Å) and Angles (deg) for **1a**, **1b**, **1c**, **2b**, **3a**, **3b**, **4b**, **5a**, **5b**

| | **1a** | **1b** | **1c** | **2b** | **3a** | **3b** | **4b** | **5a** | **5b** |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Bond Distances | | | | | |
| Ag(1)−N(11) | 2.382(3) | 2.296(3) | 2.2915(15) | 2.3394(16) | 2.326(2) | 2.427(3) | 2.326(2) | 2.365(4) | 2.351(3) |
| Ag(1)−N(21) | 2.246(3) | 2.304(3) | 2.3210(15) | 2.2701(19) | 2.290(2) | 2.233(3) | 2.304(2) | 2.267(4) | 2.275(3) |
| Ag(1)−N(31) | 2.404(3) | 2.434(3) | 2.4954(16) | 2.4081(18) | 2.471(2) | 2.310(3) | 2.285(2) | 2.311(4) | 2.296(2) |
| Ag(1)−N(41) | 2.241(3) | 2.218(4) | 2.2230(15) | 2.2478(17) | 2.226(2) | 2.306(3) | 2.372(2) | 2.343(4) | 2.380(3) |
| Ag(2)−N(51) | 2.329(3) | 2.325(3) | | | | 2.363(3) | 2.305(3) | 2.339(4) | 2.315(2) |
| Ag(2)−N(61) | 2.277(3) | 2.296(3) | | | | 2.252(3) | 2.326(3) | 2.280(4) | 2.292(2) |
| Ag(2)−N(71) | 2.343(3) | 2.413(3) | | | | 2.341(3) | 2.319(2) | 2.284(4) | 2.255(2) |
| Ag(2)−N(81) | 2.294(3) | 2.235(3) | | | | 2.263(3) | 2.339(2) | 2.354(4) | 2.389(3) |
| | | | | Bond Angles | | | | | |
| N(11)−Ag(1)−N(21) | 84.45(9) | 84.75(12) | 84.04(5) | 83.75(6) | 84.35(7) | 85.26(11) | 83.67(8) | 84.95(15) | 83.31(8) |
| N(11)−Ag(1)−N(31) | 131.85(9) | 124.92(12) | 118.71(5) | 120.38(6) | 123.44(7) | 116.23(11) | 133.39(8) | 128.07(16) | 126.55(9) |
| N(11)−Ag(1)−N(41) | 107.40(10) | 124.17(12) | 132.22(5) | 113.28(6) | 123.73(8) | 95.72(11) | 106.91(8) | 103.34(16) | 105.65(9) |
| N(21)−Ag(1)−N(31) | 114.00(10) | 98.21(12) | 95.69(5) | 111.87(6) | 99.63(7) | 126.71(12) | 124.81(8) | 124.37(16) | 128.29(9) |
| N(21)−Ag(1)−N(41) | 142.54(10) | 141.25(12) | 137.80(5) | 146.15(7) | 143.24(8) | 146.41(11) | 128.76(8) | 133.69(15) | 132.46(9) |
| N(31)−Ag(1)−N(41) | 84.85(10) | 85.81(12) | 84.92(5) | 85.40(6) | 84.58(7) | 82.85(11) | 84.13(8) | 86.16(15) | 83.96(8) |
| N(51)−Ag(2)−N(61) | 83.68(9) | 82.56(11) | | | | 84.30(11) | 84.36(9) | 85.12(16) | 84.18(8) |
| N(51)−Ag(2)−N(71) | 115.91(10) | 120.34(11) | | | | 121.65(11) | 134.19(8) | 128.05(15) | 128.44(9) |
| N(51)−Ag(2)−N(81) | 114.99(10) | 125.11(12) | | | | 113.29(11) | 113.29(9) | 105.76(16) | 103.43(9) |
| N(61)−Ag(2)−N(71) | 121.08(10) | 104.86(11) | | | | 111.99(11) | 117.58(9) | 124.09(16) | 129.62(9) |
| N(61)−Ag(2)−N(81) | 140.75(10) | 141.18(12) | | | | 146.44(11) | 127.77(9) | 130.95(15) | 129.13(9) |
| N(71)−Ag(2)−N(81) | 83.08(10) | 85.02(11) | | | | 83.82(11) | 85.60(8) | 86.74(15) | 84.45(9) |

tetradentate ligand bonding a single silver(I) cation. In the case of $\mathbf{L_m}$, the four pyrazolyl rings chelate the silver to form 16-member metallacycles. The silver resides in a distorted tetrahedral environment that is influenced by the bite angles of the bis(1-pyrazolyl)methane units. The angles restrained by the bite angles range from 83.3° to 86.7° (Table 3). The silver−nitrogen bond lengths are normal for these kinds of compounds with much less variation than those observed in the complexes of $\mathbf{L_p}$ (Table 3).[12h,13,17] With this ligand, it is clear that there are no Ag−central arene ring interactions, with central arene ring centroid distance ranging from 4.37 to 4.63Å.[18]

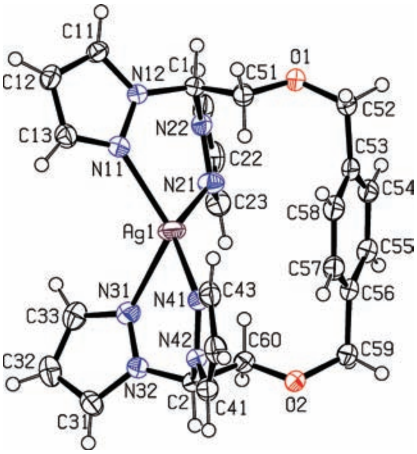

**Figure 1.** ORTEP diagrams of the cationic unit in **1c**. Displacement parameters are drawn at the 50% probability level. Hydrogen atom and some atom labels omitted for clarity.

## Discussion

Although both of the ligands $\mathbf{L_p}$ and $\mathbf{L_m}$ in the presence of metal salts have the potential to be bitopic and form coordination polymers or large metallacycles containing two metals and two ligands, they adopt a tetradentate, mononuclear metallacyclic structure when treated with silver salts. These tetradentate structures are 17- and 16-member metallacycles, respectively, in which the bis(1-pyrazolyl)methane units on both arms coordinate to a single silver(I) cation. This particular cationic motif, a metallacycle formed by one

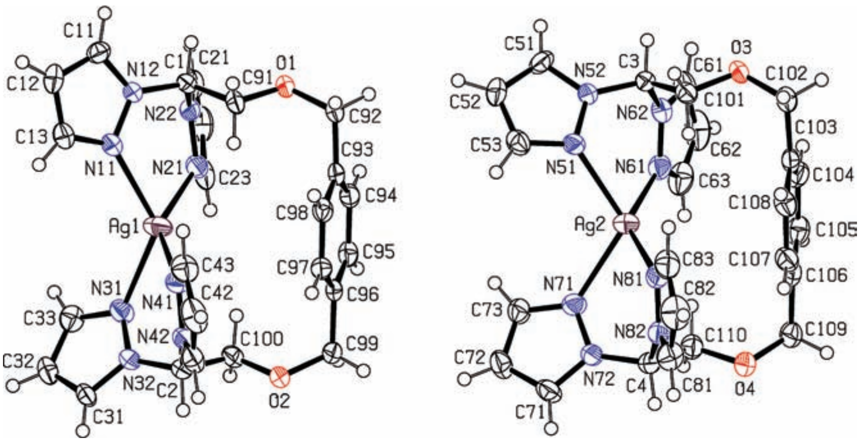

**Figure 2.** ORTEP diagrams of the two independent cationic units in **1a**. Displacement parameters are drawn at the 50% probability lever. Hydrogen atom and some atom labels omitted for clarity.

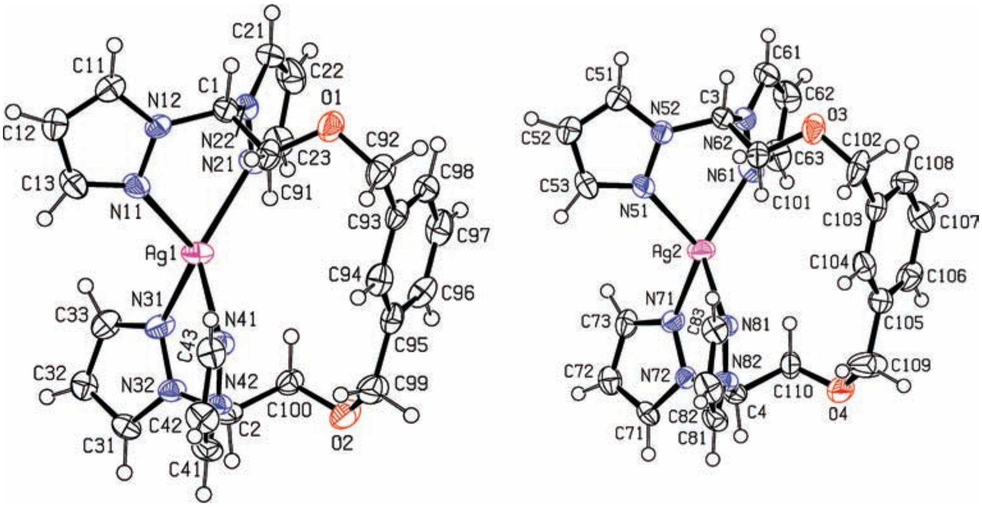

**Figure 3.** ORTEP diagrams of the two independent cationic units of **5a**. Displacement parameters are drawn at the 50% probability level. Hydrogen atom labels omitted for clarity.

**Table 4.** $\tau_4$ Parameters

| compound | silver | $\tau_4$ |
|---|---|---|
| **1a** | Ag(1) | 0.61 |
| | Ag(2) | 0.70 |
| **1b** | Ag(1) | 0.67 |
| | Ag(2) | 0.66 |
| **1c** | Ag(1) | 0.64 |
| **2b** | Ag(1) | 0.66 |
| **3a** | Ag(1) | 0.66 |
| **3b** | Ag(1) | 0.62 |
| | Ag(2) | 0.62 |
| **4b** | Ag(1) | 0.69 |
| | Ag(2) | 0.70 |
| **5a** | Ag(1) | 0.70 |
| | Ag(2) | 0.72 |
| **5b** | Ag(1) | 0.72 |
| | Ag(2) | 0.72 |

ligand and one silver, is found in all the silver compounds containing these two ligands, regardless of the counterion or the solvent used for crystallization.

The environment around the silver is a distorted tetrahedron in all of the complexes, with the smaller N—Ag—N bond angles in all of the complexes because of the restricted bite angle of the bis(1-pyrazolyl)methane units. Houser et al. have developed a paramenter, $\tau_4$, that gives a numerical value to describe the geometry of a four-coordinate system.[19] These values lie between zero and one, where zero describes a perfect square-planar arrangement and one describes a perfect tetrahedral arrangement.[19] The parameter is determined by eq 1, where α and $\beta$ are the largest angles in the four coordinate species.

$$\tau_4 = \frac{360° - (\alpha + \beta)}{141°} \qquad (1)$$

As listed in Table 4, all of the complexes have a distorted tetrahedral environment, with $\tau_4$ ranging from 0.61 to 0.70 for those containing $\mathbf{L_p}$ and from 0.69 to 0.72 for those containing $\mathbf{L_m}$. The range of $\tau_4$ for the complexes containing $\mathbf{L_m}$ are narrower and slightly higher than the range for the complexes containing $\mathbf{L_p}$ and indicate a slightly more "tetrahedral" arrangement about the silver cations. The complexes containing the $\mathbf{L_p}$ ligand also have a greater variation in Ag—N bond distances. The greater flexibility of the arms in the slightly larger rings of the $\mathbf{L_p}$ complexes likely accounts for these greater ranges in the $\tau_4$ values and Ag—N bond distances.

The structures of these silver(I) complexes of the *meta*-linked and *para*-linked bis(1-pyrazolyl)methane ligands *do not correlate* with the silver(I) complexes of the analogous *meta*- and *para*-linked tris(1-pyrazolyl)methane ligands. Most of the silver(I) complexes synthesized using these latter ligands have $\kappa^2$-$\kappa^1$ bonding of the tris(1-pyrazolyl)methane units forming complex coordination polymers.[12c,f−i] The resulting cationic structures are influenced by the counterions and the solvent of crystallization to give a variety of highly organized architectures.[12c,f−i] The one compound that does have a $\kappa^2$-$\kappa^0$ coordination mode is $\{Ag[p\text{-}C_6H_4(CH_2OCH_2CH(pz)_3)_2]PF_6\}_\infty$, which forms a helical coordination polymer.[12h] While obviously the $\mathbf{L_m}$ and $\mathbf{L_p}$ ligands reported here cannot adopt $\kappa^2$-$\kappa^1$ bonding, it was expected that these new ligands would form coordination polymers. However, the silver complexes of $\mathbf{L_m}$ and $\mathbf{L_p}$ consistently display metallacycle architecture, regardless of counterion or solvent. We find it unusual that none of the many silver(I) complexes we have reported of the *meta*- and *para*-ligands based on tris(1-pyrazolyl)methane units form this apparently very favorable mononuclear metallacyclic structure. More surprising is that coordination polymers are not observed with the $\mathbf{L_m}$ and $\mathbf{L_p}$ bis(pyrazolyl)methane ligands, but rather the metallacyclic structure is formed consistently, as reported here.

We have previously shown that the analogous *ortho*-substituted ligand, $o\text{-}C_6H_4[CH_2OCH_2CH(pz)_2]_2$, does form coordination polymers with silver(I).[13] These coordination polymers are preferred over the metallacycles because of the close proximity of the sidearms. When the sidearms are in the *ortho*-position, the *cis*-orientation, where the arms are on the same side of the ring, is less favorable than the *trans*-orientation, which gives rise to the coordination polymers rather than metallacycles. In addition, the smaller, 15 member

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[19] Yang, L.; Powell, D. R.; Houser, R. P. *Dalton Trans.* **2007**, 955.

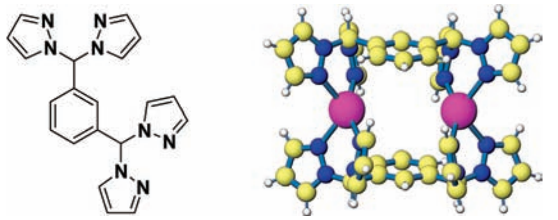

**Figure 4.** α,α,α′,α′-tetra(1-pyrazolyl)-*m*-xylene (left) and the 2:2 ligand/silver metallacycle (right).

rings that would be formed in a metallacyclic structure with this ligand may be less favorable than the 16 and 17 member rings observed in this work. The silver(I) complexes formed from this ligand and the analogous the *ortho*-linked tris(1-pyrazolyl)methane ligand form similar coordination polymers.

These silver metallacycles formed from $\mathbf{L_m}$ and $\mathbf{L_p}$ represent an unique architecture that is different from metallacycles formed by other types of ligands. There are many tetradentate chelating ligands that form what could be termed mononuclear metallacycles, but the ring size is usually limited to 6-member rings so one would view them as simple coordination compounds, not “metallacycles”.[20] Larger metallacycles found in the literature are often multimetallic and involve two or more ligands.[21] For example, we have synthesized a *meta*-linked bis(1-pyrazolyl)methane ligand that consistently forms a 2:2 ligand/silver metallacycle (Figure 4) in the presence of a variety of counterions.[17a] Clearly, the arms in this ligand are too short to form a 1:1 ligand/silver mononuclear metallacycle. Wagner has synthesized an analogous bitopic bis(1-pyrazolyl)borate ligand $[p\text{-}C_6H_4(B(pz)_2(t\text{-}Bu))_2]^{2-}$, which forms a binuclear metallacycle when treated with $MnCl_2$.[22] In this metallacycle, the manganese cations are bridged by the ligand and two chloride ions, to give a ratio 1:2:2 borate ligand/manganese/chloride.[22] There are a few examples in the literature of larger metallacycles formed by a tetradentate chelating ligand and one metal. Ward et al. describe a metallacycle formed by 1,3-bis[3-(pyridyl)1-pyrazolyl]propane ligand and $AgNO_3$. The resulting metallacycle is an 8-member ring.[23] Stille reports a 12-member ring in which palladium is chelated by 2,11-bis(diphenylphosphinomethyl)benzo[c]phenanthrene.[24] Another class of compounds, considerably different than those already described, are calix[4]arene compounds, in which different types of arms are attached in the *cis* orientation to calix[4]arene rings to chelate different metal ions.[25] A specific example with silver ions is reported by Nabeshima et al., in which two 2,2′-bipyridine moieties attached by polyether chains to a calix[4]arene are coordinated to $Ag^+$ ions.[26] In this system the 2,2′ bipyridyl rings are fixed in the *cis* orientation with respect to the calix[4]arene and form 25-member and 31-member rings with the $Ag^+$ ions. In our system the arms are free to orient *trans* to one another, as demonstrated by the *ortho*-linked ligand, but choose the *cis* orientation for $\mathbf{L_m}$ and $\mathbf{L_p}$ to form the metallacyclic structures observed.

Another difference between silver(I) complexes containing the tris(1-pyrazolyl)methane units versus the bis(1-pyrazolyl)methane units is the behavior in acetonitrile solutions. In the silver(I) complexes reported here, as well as previously published silver(I) complexes containing bitopic bis(1-pyrazolyl)methane units,[13,17] all of the $^1H$ NMR spectra in acetonitrile are shifted downfield compared to the free ligand. However, in the case of silver(I) complexes of analogous ligands containing tris(1-pyrazolyl)methane units, the $^1H$ NMR spectra in acetonitrile are identical to the free ligand,[12g,h] clearly indicating that the solvent has displaced the ligand. With this new family of ligands, the coordination of the bis(1-pyrazolyl)methane unit to silver(I) in solutions of acetonitrile resists displacement better than the tris(1-pyrazolyl)methane unit.

We have designed these *para*- and *meta*- linked bis(1-pyrazolyl)methane ligands to be semiflexible to maximize non-covalent interactions. However, in comparison to our previously published results the flexibility of these ligands in the resulting metallacycle is significantly limited by the formation of the ring. Although the metallacycles are organized by $\pi-\pi$ interactions, $C-H\cdots\pi$ interactions, and in one case (**3a**) $C-H\cdots O$ interactions (see Supporting Information), there is not a dominant supramolecular motif evident in the extended structures. The consistent formation of the metallacycle, regardless of solvent or anion, demonstrates that the molecular structure is not heavily influenced by non-covalent interactions. In contrast, in our previously published results with the *ortho*-linked ligand built from bis(1-pyrazolyl)methane units and the larger family of tris(1-pyrazolyl)methane ligands, the molecular structures appear to be greatly impacted by the non-covalent interactions.

## Conclusion

The structures of the silver(I) complexes of the bis(1-pyrazolyl)methane based ligands $p\text{-}C_6H_4[CH_2OCH_2CH(pz)_2]_2$ ($\mathbf{L_p}$) and $m\text{-}C_6H_4[CH_2OCH_2CH(pz)_2]_2$ ($\mathbf{L_m}$) are all mononuclear metallacycles. In these metallacycles, the $\mathbf{L_p}$ or $\mathbf{L_m}$ ligands are tetradentate, chelating one silver ion, to give 17- or 16-member rings, respectively. The formation of the metallacycle is the dominant feature in all of the crystal structures containing the $\mathbf{L_p}$ or $\mathbf{L_m}$ ligand, regardless of solvent or anion. This consistency in overall structure with variation in counterions and solvent is markedly different from the structures observed with the analogous tris(1-pyrazolyl)methane ligands, where the architectures are influenced by these factors. Compounds of the tris(1-pyrazolyl)methane ligands also display much more complex supramolecular structures than the complexes formed by $\mathbf{L_p}$ and $\mathbf{L_m}$, presumably because of the limited flexibility afforded by the metallacyclic structure of the latter. The structures of $\mathbf{L_p}$ and $\mathbf{L_m}$ complexes are also very different from those formed by the analogous *ortho*-substituted, bis(1-

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pyrazolyl)methane based ligand, *o*-$C_6H_4[CH_2OCH_2CH(pz)_2]_2$, where the formation of coordination polymers dominates. The mononuclear, metallacycle structures of the silver(I) complexes of the new ligands reported here represent a unique architecture. The ring size is between those commonly found for classical chelating ligands, around 6, and larger, systems of greater than 25.

**Acknowledgment.** We thank the National Science Foundation (CHE-0715559) for financial support.

**Supporting Information Available:** Further details are given in Figures S1−S11. This material is available free of charge via the Internet at http://pubs.acs.org.

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