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Synthesis and Spectroscopic Characterization of Silver(I) Complexes with the Bis(1,2,4-triazol-1-yl)alkane Ligand $tz_2(CH_2)$. X-ray Structures of Two- and Three-Dimensional Coordination Polymers

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1:1 $AgX:tz_2(CH_2)$ ($X = NO_3$, NO_2, ClO_4), 3:4 ($X = O_3SCF_3$ (=OTf), O_2CCF_3 (= tfa)), and 2:1 adducts ($X = BrO_3$) have been synthesized and characterized in the solid state and in solution by analyses, spectral (IR, far-IR, ^1H and ^{13}C NMR, ESI MS) data, and conductivity measurements. The crystal structures of the 1:1 $AgNO_3:tz_2(CH_2)$ and $AgNO_2:tz_2(CH_2)$ adducts determined by X-ray studies show that $tz_2(CH_2)$ coordinates to silver through the exodentate nitrogen atoms at the 4-positions of the triazole rings, yielding neutral polymers, while the ionic $Ag(OTf):tz_2(CH_2)$ (3:4) adduct has a three-dimensional polymeric cation. The NMR and ESI MS data suggest that $tz_2(CH_2)$ is only weakly coordinating, adducts between Ag(I) and CH_3CN being more prevalent in acetonitrile solution.

Introduction

Following the initial reports on poly(pyrazolyl)borate ligands by Trofimenko, a large number of papers have appeared on the coordination chemistry of azole-containing donors.[1] Modifications of polypyrazolylborates can be made by replacement of the boron bridging atom with carbon,[2] silicon,[3] or phosphorus.[4] Other important variations can be effected by changing the substituents on the heterocyclic ring or by replacement of the pyrazolyl with triazolyl,[5] imidazolyl,[6] and methimazolyl moieties.[7]

Poly(triazolyl)borate ligands with their diverse bonding centers give rise to an interesting coordination chemistry and supramolecular architecture possibilities in the solid state with the formation of, e.g., incorporated two-dimensional water layers and linkage isomerism;[8] an increasing interest has been devoted to the controlled synthesis of inorganic

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(1) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, 1999. Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943−980.

(2) Trofimenko, S. *J. Am. Chem. Soc.* **1970**, *92*, 5118−5126. Claramunt, R. M.; Domiano, P.; Elguero, J.; Lavandera, J. L. *Bull. Soc. Chim. Fr.* **1989**, *4*, 472−476. Pettinari, C.; Lorenzotti, A.; Sclavi, G.; Cingolani, A.; Rivarola, E.; Colapietro, M.; Cassetta, A. *J. Organomet. Chem.* **1995**, *496*, 69−85.

(3) Klanberg, F., *personal communication*, ref 177 in: The coordination chemistry of pyrazole-derived ligands. Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497−509. Pullen, E. E.; Rheingold, A. L.; Rabinovich, D. *Inorg. Chem. Commun.* **1999**, *2*, 194−196. Pullen, E. E.; Rabinovich, D.; Incarvito, C. D.; Concolino, T. E.; Rheingold, A. L. *Inorg. Chem.* **2000**, *39*, 1561−1567. Richburg, L. M.; Farouq, J. A.; Incarvito, C. D.; Rheingold, A. L.; Rabinovich, D. *Polyhedron* **2000**, *19*, 1815−1820.

(4) Joshi, V. S.; Kale, V. K.; Sathe, K. M.; Sarkar, A.; Tavale, S. S.; Suresh, C. G. *Organometallics* **1991**, *10*, 2898−2902. Psillakis, E.; Jeffery, J. C.; McCleverty, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1997**, 1645−1651.

(5) Janiak, C.; Scharmann, T. G.; Green, J. C.; Parkin, R. P. G.; Kolm, M. J.; Riedel, E.; Mickler, W.; Elguero, J.; Claramunt, R. M.; Sanz, D. *Chem. Eur. J.* **1996**, *2*, 992−1000.

(6) Zaidi, S. A. A.; Khan, T. A. *Synth. React. Inorg. Met.-Org. Chem.* **1984**, *14*, 717−729. Janiak, C.; Temidzemir, S.; Röhr, C. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1265−1267.

(7) Kimblin, C.; Hascall, T.; Parkin, G. *Inorg. Chem.* **1997**, *36*, 5680−5681. Reglinski, J.; Garner, M.; Cassidy, I. D.; Slavin, P. A.; Spicer, M. D.; Armstrong, D. R. *J. Chem. Soc., Dalton, Trans.* **1999**, 2119−2126. Kimblin, C.; Bridgewater, B. M.; Hascall, T.; Parkin, G. *J. Chem. Soc., Dalton Trans.* **2000**, 891−897. Santini, C.; Pellei, M.; Gioia Lobbia, G.; Pettinari, C.; Drozdov, A.; Troyanov, S. *Inorg. Chim. Acta* **2001**, *325*, 20−28. Cassidy, I.; Garner, M.; Kennedy, A. R.; Potts, G. B. S.; Reglinski, J.; Slavin, P. A.; Spicer, M. D. *Eur. J. Inorg. Chem.* **2002**, 1235−1239. White, J. L.; Tanski, J. M.; Rabinovich, D. *J. Chem. Soc., Dalton Trans.* **2002**, 2987−2991. Bakbak, S.; Incarvito, C. D.; Rheingold, A. L.; Rabinovich, D. *Inorg. Chem.* **2002**, *41*, 998−1001. Garcia, R.; Domingos, A.; Paulo, A. Santos, I.; Alberto, R. *Inorg. Chem.* **2002**, *41*, 2422−2428.

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materials with inner cavities for the catalysis of organic reactions[9] or with collective magnetic phenomena for the design of molecular-based ferromagnets.[10] In our research concerning modifications of the poly(pyrazolyl)borate ligands in which the pyrazolyl rings are replaced by 1,2,4-triazolyl or imidazolyl rings, some interesting single strand silver(I) coordination polymers containing bridging poly(1-imidazolyl)borates have been reported.[11]

Although substititutions of triazole for pyrazole in poly(pyrazolyl)alkanes to form poly(triazolyl)alkanes have been reported by Trofimenko in 1967[12] and by Elguero and coworkers 20 years ago,[13] only a few examples of coordination compounds containing $tz_{4-n}CH_n$ have been reported. The coordination chemistry of poly(triazolyl)alkanes is notably underdeveloped, perhaps because of the ready formation of polymeric insoluble species.[14] These include some diorganotin(IV) complexes which are linkage coordination polymers in which tz_2CH_2 acts as a bridging instead of chelating ligand,[15] some group-6 metal carbonyl complexes in which 3,5-$Me_2tz_2CH_2$ acts as a chelating bidentate ligand with two endodentate nitrogen atoms,[16] and a 1,2-$tz_2(CH_2)_2$ copper(I) compound in which the ligand coordinates through exo-nitrogen atoms in the azole rings.[17] Tang has also reported the formation of heterobimetallic complexes containing diorganotin(IV) dihalides and group-6 metal carbonyls.[16]

In this paper we describe the synthesis of two- and three-dimensional coordination polymers from tz_2CH_2 with Ag(I) cations, their spectroscopic properties, and the results of some single-crystal X-ray studies.

Experimental Section

General Procedures. All reactions were carried out protected from light under an atmosphere of dry oxygen-free dinitrogen, using standard Schlenk techniques. Solvents were used as supplied or distilled by using standard methods. All chemicals were purchased from Aldrich (Milwaukee) and used as received. The donor $tz_2(CH_2)$ was synthesized by the procedure previously reported[14] and purified by several recrystallizations from chloroform/hexane. Solvents were dried by standard techniques. The samples were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). Elemental analyses (C, H, N, S) were performed with a Fisons Instruments 1108 CHNS−O Elemental analyzer. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin-Elmer System 2000 FT-IR instrument. ^1H, ^{19}F, and ^{13}C NMR spectra were recorded on a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^1H, 282.2 MHz for ^{19}F, and 75 MHz for ^{13}C). H and C chemical shifts are reported in ppm vs $SiMe_4$, F chemical shifts in ppm vs $CFCl_3$. The electrical conductances of the acetone and acetonitrile solutions were measured with a Crison CDTM 522 conductimeter at room temperature. The positive and negative electrospray mass spectra were obtained with a Series 1100 MSI detector HP spectrometer, using a acetonitrile mobile phase. Solutions (3 mg/mL) for electrospray ionization mass spectrometry (ESI-MS) were prepared by using reagent grade acetone or acetonitrile. For the ESI-MS data, masses and intensities were compared to those calculated by using the IsoPro isotopic abundance simulator version 2.1;[18] peaks containing silver(I) ions are identified as the centers of isotopic clusters.

Syntheses of Complexes. *$(AgNO_3)$:$tz_2(CH_2)$ (1:1) (**1**).* To a solution of $tz_2(CH_2)$ (0.150 g, 1.0 mmol) in ethanol (30 mL) was added an ethanol solution of $AgNO_3$ (0.169 g, 1.0 mmol) in the same solvent (10 mL). The mixture was stirred at 50 °C for 2 h. It was then cooled and left at 4 °C until a colorless crystalline solid was formed, which was filtered off, washed with diethyl ether, and dried to constant weight under reduced pressure (0.254 g, 0.8 mmol, 80% yield). Mp 149−151 °C. Anal. Calcd for $C_5H_6AgN_7O_3$: C, 18.77; H, 1.89; N, 30.64%. Found: C, 18.58; H, 2.04; N, 30.32%. IR (Nujol, cm^{-1}) data: 3112 m, 3089 w, $\nu(C_{arom}-H)$, 1839 m, 1824 m, 1789 m, 1749 m, 1741 m, 1648 s, 1641 s $\nu(NO_3)$, 1515 vs, $\nu(C=C) + \nu(C=N)$, 1372 br, 1350 br, 1270 s br, 1199 s, $\nu(NO_3)$, 408 m, 398 m, 314 w, 308 w, 290 w, 280 w, $\nu(Ag-O) + \nu(Ag-N)$. ^1H NMR (CD_3CN, 298K): δ, 6.49 (s, 2 H, CH_{2tz}), 7.95 (s, 2 H, $H\text{-}5_{tz}$), 8.59 (s, 2 H, $H\text{-}3_{tz}$). $^{13}C\{^1H\}$ NMR (CD_3CN, 298 K): δ 60.82 (s, CH_{2tz}), 146.01 (s, $C5-H_{tz}$), 153.5 (s, $C3-H_{tz}$). Λ_m (CH_3CN, 10^{-3} M, 298 K): 137 Ω^{-1} cm^2 mol^{-1}. ESI MS (CH_3CN, 10^{-4} M) (+): 147 (30) $[Ag(CH_3CN)]^+$, 189 (100) $[Ag(CH_3CN)_2]^+$, 298 (40) $[Ag(tz_2(CH_2)(CH_3CN)_2]^+$, 359 (10) $[Ag_2(CH_3CN)_2(NO_3)]^+$, 407 (18) $[Ag(tz_2(CH_2))_2]^+$, 468 (8) $[Ag_2(CH_3CN)(tz_2(CH_2))(NO_3)]^+$. (−) 62 (100) $[NO_3]^-$, 231 (50) $[Ag(NO_3)_2]^-$, 365 (30) $[Ag_2(NO_3)(H_2O)Cl_2]^-$, 401 (18) $[Ag_2(NO_3)_3]^-$.

*$(AgNO_2)$:$tz_2(CH_2)$ (1:1) (**2**).* To a 1:1 ethanol/acetonitrile solution (30 mL) of $tz_2(CH_2)$ (0.150 g, 1.0 mmol) $AgNO_2$ (0.153 g, 1.0 mmol) was added. The mixture was stirred at room temperature for 2 h. It was then cooled and left at 4 °C until a colorless crystalline solid was formed, which was filtered off, washed with diethyl ether, and dried to constant weight under reduced pressure (0.270 g, 0.9 mmol, 90% yield). Mp 164−168 °C. Anal. Calcd for $C_5H_6AgN_7O_2$: C, 19.62; H, 2.63; N, 32.04%. Found: C, 19.92; H, 2.54; N, 32.19%. IR (Nujol, cm^{-1}): 3111 m, 3090 w, 3026 w, $\nu(C_{arom}-H)$, 1503 vs, $\nu(C=C) + \nu(C=N)$, 1236 s, 1199 m, 1130 m, $\nu(N-O)$, 887 m $\delta(ONO)$ 419 w, 390 sh, 353 w, 327 w, 309 w, 303 w, 278 w, 266 w, $\nu(Ag-O) + \nu(Ag-N)$. ^1H NMR (DMSO-d_6, 295K): δ 6.68 (s, 2 H, CH_{2tz}), 8.07 (s, 2 H, $H\text{-}5_{tz}$), 8.90 (s, 2 H, $H\text{-}3_{tz}$). ^1H NMR (CD_3CN, 295K): δ 6.47 (s, 2 H, CH_{2tz}), 7.93 (s, 2 H, $H\text{-}5_{tz}$), 8.54 (s, 2 H, $H\text{-}3_{tz}$). $^{13}C\{^1H\}$ NMR (CD_3CN, 295K): δ 60.74 (s, CH_{2tz}), 145.82 (s, $C5_{tz}$), 153.63 (s, $C3_{tz}$). Λ_m (CH_3CN, 10^{-3} M, 298 K): 137 Ω^{-1} cm^2 mol^{-1}. ESI MS (CH_3CN, $10-^4$ M) (+): 189 (100) $[Ag(CH_3CN)_2]^+$, 298 (40) $[Ag(tz_2(CH_2)(CH_3CN)_2]^+$. (−): 62 (5) $[NO_3]^-$, 199 (7) $[Ag(NO_2)_2]^-$, 333 (18) $[Ag_2(NO_2)_2Cl]^-$, 354 (18) $[Ag_2(NO_2)_3]^-$.

*$(AgBrO_3)$:$tz_2(CH_2)$ (2:1) (**3**).* To a 1:1 ethanol/acetonitrile solution (30 mL) of $tz_2(CH_2)$ (0.150 g, 1.0 mmol) a solution of $AgBrO_3$

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(8) Janiak, C.; Scharmann, T. G.; Hemling, H.; Lentz, D.; Pickardt, J. *Chem. Ber.* **1995**, *128*, 235−244.

(9) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151−1152; Ibrahim, A. M. A.; Soliman, T. M.; Etaiw, S. E. H.; Fischer, R. D. *J. Organomet. Chem.* **1994**, *468*, 93−98.

(10) De Munno, G.; Julve, M.; Nicolo, F.; Lloret, F.; Faus, J.; Ruiz, R.; Sinn, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 613−615.

(11) Effendy; Gioia Lobbia, G.; Pellei, M.; Pettinari, C.; Santini, C.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2001**, 528−534.

(12) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170−3177.

(13) Julia, S.; Sala, P.; Mazo, J. D.; Sancho, M.; Ochoa, C.; Elguero, J.; Fayet, J. P.; Vertut, M. C. *J. Heterocycl. Chem.* **1982**, *19*, 1141−1145.

(14) Gioia Lobbia, G.; Bonati, F.; Cingolani, A.; Leonesi, D.; Lorenzotti, A. *Synth. React. Inorg. Met. Org. Chem.* **1988**, *18*, 535−550. Pettinari, C. *Main Group Met. Chem.* **1996**, *19*, 489−498.

(15) Tang, L. F.; Wang, Z.-H.; Chai, J. F.; Jia, W.-L.; Xu, Y.-M.; Wang, J.-T. *Polyhedron* **2000**, *19*, 1949−1954.

(16) Tang, L. F.; Wang, Z. H.; Chai, J. F.; Leng, X. B.; Wang, J. T.; Wang, H. G. *J. Organomet. Chem.* **2002**, *642*, 179−185.

(17) Carcia, Y.; van Koningsbruggen, P. J.; Kooijman, H.; Spek, A. L.; Haasnoot, J. G.; Kahn, O. *Eur. J. Inorg. Chem.* **2000**, 307−314.

(18) Senko, M. W. National High Magnetic Field Laboratory.

(0.236 g, 1.0 mmol) in the same solvent (10 mL) was added. The mixture was stirred at room temperature for 2 h. A colorless solid slowly deposited, which was filtered off, washed with diethyl ether, and dried to constant weight under reduced pressure (0.230 g, 0.37 mmol, 74% yield). Mp 178−182 °C. Anal. Calcd for $C_5H_6Ag_2Br_2N_6O_6$: C, 9.66; H, 0.97; N, 13.52%. Found: C, 9.92; H, 1.14; N, 13.89%. IR (Nujol, cm^{-1}): 3112 m, 3078 w, $\nu(C_{arom}-H)$, 1518 vs, $\nu(C{=}C) + \nu(C{=}N)$, 1370 s, 1204 s, $\nu(BrO_3)$, 419 m, 411 m, 395 m, 355 s, 304 w, 280 w $\nu(Ag-O) + \nu(Ag-N)$. ^1H NMR (DMSO-d_6, 295 K): δ 6.69 (s, 2 H, CH_{2tz}), 8.09 (s, 2 H, $H\text{-}5_{tz}$), 8.90 (s, 2 H, $H\text{-}3_{tz}$). ^1H NMR (CD_3CN, 298 K): δ 6.46 (s, 2 H, CH_{2tz}), 7.93 (s, 2 H, $H\text{-}5_{tz}$), 8.53 (s, 2 H, $H\text{-}3_{tz}$). $^{13}C\{^1H\}$ NMR (CD_3CN, 295K): δ, 60.51 (s, CH_{2tz}), 145.79 (s, $C5_{tz}$), 153.59 (s, $C3_{tz}$). Λ_m (CH_3CN, 0.9×10^{-3} M, 298 K): 159 Ω^{-1} cm^2 mol^{-1}. ESI MS (CH_3CN, 10^{-4} M) (+): 147 (10) $[Ag(CH_3CN)]^+$, 189 (100) $[Ag(CH_3CN)_2]^+$, 298 (40) $[Ag(tz_2(CH_2)(CH_3CN)_2]^+$. (−): 127 (100) $[BrO_3]^-$.

(AgClO$_4$):tz$_2$(CH$_2$) (1:1) (**4**). To a solution of $tz_2(CH_2)$ (0.150 g, 1.0 mmol) in ethanol (30 mL), $AgClO_4$ (0.21 g, g, 1.0 mmol) was added. The mixture was stirred at room temperature for 2 h. A pale pink solid slowly formed, which was filtered off, washed with diethyl ether, and dried to constant weight under reduced pressure (0.283 g, 0.83 mmol, 83% yield). Mp 284−288 °C. Anal. Calcd for $C_5H_6AgClN_6O_4$: C, 16.80; H, 1.69; N, 23.51%. Found: C, 16.73; H, 1.67; N, 23.19%. IR (Nujol, cm^{-1}) data: 3121 s, 3022 m, $\nu(C_{arom}-H)$, 1520 vs, $\nu(C{=}C) + \nu(C{=}N)$, 1105 vs, 1080 s br, 1050 s br, $\nu_3(ClO_4)$, 622 vs, $\nu_4(ClO_4)$, 389 w, 352 w, 327 w, 302 w, 280 w, 246 w, 226 w $\nu(Ag-O) + \nu(Ag-N)$. ^1H NMR (CD_3CN, 298 K): δ 6.50 (s, 2 H, CH_{2tz}), 7.97 (s, 2 H, $H\text{-}5_{tz}$), 8.62 (s, 2 H, $H\text{-}3_{tz}$). $^{13}C\{^1H\}$ NMR (CD_3CN, 295 K): δ 61.00 (s, CH_{2tz}), 146.27 (s, $C5_{tz}$), 153.43 (s, $C3_{tz}$). Λ_m (CH_3CN, 1.0×10^{-3} M, 298 K): 142 Ω^{-1} cm^2 mol^{-1}. ESI MS (CH_3CN, 10^{-4} M) (+): 189 (100) $[Ag(CH_3CN)_2]^+$, 298 (10) $[Ag(tz_2(CH_2)(CH_3CN)_2]^+$. (−): 99 (100) $[ClO_4]^-$, 220 (7) $[Na(ClO_4)_2]^-$, 306 (10) $[Ag(ClO_4)_2]^-$.

(Ag(OTf)):tz$_2$(CH$_2$) (3:4) (**5**). Compound **5** was synthesized similarly to **4** in 80% yield. Mp 250−254 °C. Anal. Calcd for $C_{23}H_{24}Ag_3F_9N_{24}O_9S_3$: C, 20.14; H, 1.76; N, 24.51; S, 7.01. Found: C, 20.32; H, 1.85; N, 24.73; S, 7.43%. IR (Nujol, cm^{-1}) data: 3126 vs, 3036 m, $\nu(C_{arom}-H)$, 1510 vs, $\nu(C{=}C) + \nu(C{=}N)$, 1261 vs, 1216, 1160 s, 1012 s, 970s, $\nu(SO_3CF_3)$, 399 m, 383 sh, 349 w, 317 w, 211 w $\nu(Ag-O) + \nu(Ag-N)$. ^1H NMR (CD_3CN, 295K): δ 6.49 (s, 2 H, CH_{2tz}), 7.95 (s, 2 H, $H\text{-}5_{tz}$), 8.59 (s, 2 H, $H\text{-}3_{tz}$). ^1H NMR ($CDCl_3$, 295 K): δ 6.46 (s, 2 H, CH_{2tz}), 8.00 (s, 2 H, $H\text{-}5_{tz}$), 8.45 (s, 2 H, $H\text{-}3_{tz}$). $^{13}C\{^1H\}$ NMR (CD_3CN, 295K): δ 60.81 (s, CH_{2tz}), 146.00 (s, $C5_{tz}$), 153.38 (s, $C3_{tz}$). $^{19}F\{^1H\}$ NMR (CD_3CN, 293 K): δ 98.4 (s, CF_3). Λ_m (CH_3CN, 1.0×10^{-3} M, 298 K): 139 Ω^{-1} cm^2 mol^{-1}. ESI MS (CH_3CN, 10^{-4} M) (+): 147 (10) $[Ag(CH_3CN)]^+$, 189 (100) $[Ag(CH_3CN)_2]^+$, 298 (18) $[Ag(tz_2(CH_2)(CH_3CN)_2]^+$, 407 (5) $[Ag(tz_2(CH_2))_2]^+$, 555 (8) $[Ag_2(tz_2(CH_2))(CH_3CN)(O_3SCF_3)]^+$, 665 (5) $[Ag_2(tz_2(CH_2))_2(O_3SCF_3)]^+$, 922 (5) $[Ag_3(tz_2(CH_2))_2(O_3SCF_3)_2]^+$, 1328 (3) $[Ag_4(tz_2(CH_2))_3(O_3SCF_3)_3]^+$, 1586 (1) $[Ag_5(tz_2(CH_2))_3(O_3SCF_3)_4]^+$. (−): 149 (100) $[O_3SCF_3]^-$, 320 (10) $[Na(O_3SCF_3)_2]^-$, 407 (10) $[Ag(O_3SCF_3)_2]^-$.

(Ag(tfa)):tz$_2$(CH$_2$) (3:4) (**6**). Compound **6** was obtained similarly to **4** in 77% yield. Mp 177−180 °C. Anal. Calcd for $C_{26}H_{24}Ag_3F_9N_{24}O_6$: C, 24.72; H, 1.91; N, 26.61%. Found: C, 24.54; H, 2.01; N, 26.52%. IR (Nujol) data: 3110 w, 3086 m, $\nu(C_{arom}-H)$, 1690 vs, $\nu_{as}(COO)$, 1508 vs, $\nu(C{=}C) + \nu(C{=}N)$, 1200 vs, 1164 vs, 1127 vs, $\nu(CF_3)$, 406 m, 396 w, 380 m, 357 w, 265 m $\nu(Ag-O) + \nu(Ag-N)$. ^1H NMR ($CDCl_3$, 295 K): δ 6.46 (s, 2 H, CH_{2tz}), 8.0 (br, 2 H, $H\text{-}5_{tz}$), 8.5 (br, 2 H, $H\text{-}3_{tz}$). ^1H NMR (CD_3CN, 295 K): δ 6.52 (s, 2 H, CH_{2tz}), 7.96 (s, 2 H, $H\text{-}5_{tz}$), 8.66 (s, 2 H, $H\text{-}3_{tz}$). $^{13}C\{^1H\}$ NMR (CD_3CN, 295 K): δ 60.87 (s, CH_2 tz$_2$), 146.18 (s, $C5\text{-}H_{tz}$), 153.55 (s, $C3\text{-}H_{tz}$), $^{19}F\{^1H\}$ NMR (CD_3CN, 298 K): δ, 103.0 (s, $OOCCF_3$). Λ_m (CH_3CN, 1.0×10^{-3} M, 298 K): 137 Ω^{-1} cm^2 mol^{-1}. ESI MS (CH_3CN, 10^{-4} M) (+): 147 (10) $[Ag(CH_3CN)]^+$, 189 (100) $[Ag(CH_3CN)_2]^+$, 298 (30) $[Ag(tz_2(CH_2)(CH_3CN)_2]^+$, 407 (18) $[Ag(tz_2(CH_2))_2]^+$, 628 (10) $[Ag_2(tz_2(CH_2))_2(O_2CCF_3)]^+$. (−): 113 (100) $[O_2CCF_3]^-$, 332 (50) $[Ag(O_2CCF_3)_2]^-$, 554 (10) $[Ag_2(O_2CCF_3)_3]^-$, 774 (13) $[Ag_3(O_2CCF_3)_4]^-$.

Structure Determinations. Full spheres of "low-temperature" CCD area-detector diffractometer data were measured (Bruker AXS instrument, ω-scans, T ca. 153 K; monochromatic Mo Kα radiation, $\lambda = 0.710\,73$ Å) yielding N_t(total) reflections, these merging to N unique (R_{int} quoted) after multiscan/"empirical" absorption correction (proprietary software); N_o with $F > 4\sigma(F)$ were used in the full matrix least squares refinements, refining anisotropic thermal parameter forms for the non-hydrogen atoms, $(x, y, z, U_{iso})_H$ constrained at estimates unless otherwise noted. Conventional residuals R, R_w (weights: $((\sigma^2(F) + 0.0004F^2)^{-1})$ on $|F|$ are cited at convergence; neutral atom complex scattering factors were employed within the context of the Xtal 3.7 program system.[19] Pertinent results are given below and in the tables and figures, the latter showing 50% displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. Individual diversities in procedure (etc.) are noted as "variata".

Crystal/Refinement Data. *tz$_2$(CH$_2$)* $\equiv C_5H_6N_6$, $M = 150.2$. Monoclinic, space group $P2/n$ (C_{2h}^4, No. 13 (variant)), $a = 12.529(1)$, $b = 4.1809(4)$, $c = 13.105(1)$ Å, $\beta = 101.030(2)°$, $V = 673.8$ Å^3. D_c ($Z = 4$) $= 1.480$ g cm^{-3}. $\mu_{Mo} = 0.11$ mm^{-1}; specimen $0.5 \times 0.5 \times 0.35$ mm (no correction). $2\theta_{max} = 75°$; $N_t = 13\,729$, $N = 3528$ ($R_{int} = 0.025$), $N_o = 2980$; $R = 0.038$, $R_w = 0.049$. $|\Delta\rho_{max}| = 0.33(3)$ e Å^{-3}. $(x, y, z, U_{iso})_H$ refined.

1. AgNO$_3$:tz$_2$(CH$_2$) (1:1) $\equiv C_5H_6AgN_7O_3$, $M = 320.0$. Orthorhombic, space group $Pna2_1$ (C_{2v}^9, No. 33), $a = 7.1605(5)$, $b = 14.179(1)$, $c = 9.0770(6)$ Å, $V = 921.6$ Å^3. D_c ($Z = 4$) $= 2.306$ g cm^{-3}. $\mu_{Mo} = 2.2$ mm^{-1}; specimen: $0.30 \times 0.20 \times 0.06$ mm; $'T_{min,max} = 0.57, 0.86$. $2\theta_{max} = 75°$; $N_t = 18350$, $N = 2501$ ($R_{int} = 0.026$), $N_o = 2380$; $R = 0.018$, $R_w = 0.024$. $|\Delta\rho_{max}| = 0.79(4)$ e Å^{-3}. $(x, y, z, U_{iso})_H$ refined.

2. AgNO$_2$:tz$_2$(CH$_2$) (1:1) $\equiv C_5H_6AgN_7O_2$, $M = 304.0$. Monoclinic, space group $P2_1$ (C_2^2, No. 4), $a = 7.5425(6)$, $b = 13.120(1)$, $c = 9.4021(7)$ Å, $\beta = 101.005(2)°$, $V = 913.3$ Å^3. D_c ($Z = 4$) $=$ 2.211 g cm^{-3}. $\mu_{Mo} = 2.2$ mm^{-1}; specimen $0.15 \times 0.13 \times 0.11$ mm; $'T_{min,max} = 0.67, 0.86$. $2\theta_{max} = 75°$; $N_t = 17106$, $N = 4769$ ($R_{int} = 0.020$), $N_o = 4276$; $R = 0.032$, $R_w = 0.037$. $|\Delta\rho_{max}| = 2.29(8)$ e Å^{-3}.

Variata. In both this and the following structure Friedel data were preserved distinct; in this case, refinement of x_{abs} was indeterminate of chirality and, accordingly, data were merged in the final least squares cycles.

5. AgOTf:tz$_2$(CH$_2$) (3:4)·MeCN $= C_{25}H_{27}Ag_3F_9N_{25}O_9S_3$, $M = 1412.4$. Orthorhombic, space group $P2_12_12_1$ (D_2^4, No. 19), $a = 10.685(1)$, $b = 11.821(1)$, $c = 36.625(4)$ Å, $V = 4626$ Å^3. D_c ($Z = 4$) $= 2.02_8$ g cm^{-3}. $\mu_{Mo} = 1.5$ mm^{-1}; specimen $0.22 \times 0.09 \times 0.07$ mm; $'T_{min,max} = 0.64, 0.86$. $2\theta_{max} = 58°$; $N_t = 45716$, $N = 6522$ ($R_{int} = 0.057$), $N_o = 4546$; $R = 0.050$, $R_w = 0.051$. $|\Delta\rho_{max}| = 1.1(1)$ e Å^{-3}. $x_{abs} = 0.13(5)$.

Results and Discussion

Syntheses. Derivatives **1**−**6** were synthesized by the interaction of bis(triazol-1-yl)methane $tz_2(CH_2)$ with silver(I)

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(19) Hall, S. R.; du Boulay, D. J.; Olthof-Hazekamp, R., Eds. *The Xtal 3.7 System*; University of Western Australia, 2001.

salts AgX (X = NO_3, NO_2, BrO_3, ClO_4, OTf, or tfa) in ethanol or ethanol:acetonitrile 1:1 solution (eq 1).

$$tz_2(CH_2) + AgX \rightarrow (AgX){:}tz_2(CH_2)\ (n{:}m) \qquad (1)$$

where $n = 1$, $m = 1$, X = NO_3, NO_2, ClO_4; $n = 2$, $m = 1$, X = BrO_3; $n = 3$, $m = 4$, X = tfa, OTf.

Complexes **1**−**6** can be obtained as colorless crystals, **5** with acetonitrile of crystallization, upon slow interdiffusion of solutions of reactants. No adducts were afforded under the same conditions when silver(I) halides were employed as acceptors. In addition no formation of adducts has been observed in more ionizing solvents such as acetone or DMSO. The stoichiometries found are independent of the ligand-to-metal ratio employed. For example, adduct **3** having a ligand-to-metal ratio 1:2 was obtained even when a large excess of $tz_2(CH_2)$ was used.

Some of these complexes were slightly soluble in chlorinated solvents but more soluble in oxygenated solvents such as acetone and DMSO. Even in the solid state compounds **5** and **6** were prone to absorb ambient water, while the other compounds were stable and not hygroscopic. Compounds **5** and **6** were also prone to absorb molecules of solvent from CH_3CN solution from which they can be recrystallized. Compounds **1**−**6** exhibit conductivity values typical of electrolytic species according to eq 2.

$$AgX{:}tz_2(CH_2)\ (n{:}m) + xCH_3CN \rightleftharpoons n[Ag(CH_3CN)_x] + nX^- + mtz_2(CH_2) \qquad (2)$$

In the IR spectra of all compounds the ring breathing vibrations fall between 1540 and 1510 cm^{-1}. Derivative **1** contains a five-coordinate geometry in the solid state with the counterion NO_3^- μ^2-bridging via a single oxygen atom. The IR data are in accordance with this evidence; in particular the combination band $\nu_1 + \nu_4$ is split (1749 and 1741 cm^{-1}) with $\Delta = 8$ cm^{-1}, typical of strongly asymmetric bridging bidentate or unidentate nitrate.[20] The nitrite behavior in **2** is not well identified due to the presence in the solid spectra of several overlapped absorptions in the region 900−1500 cm^{-1}, but the existence of AgN_4 and $AgNO_4$ cores (see below) seems to be supported by the presence of weak to medium absorptions in the range 150−350 cm^{-1} ascribed to M−O and M−N stretching vibrations.[21] The spectroscopic behavior of the perchlorate derivative **4** is typical of an ionic compound containing an outer-sphere group, only two absorptions being found at ca. 1090 and 620 cm^{-1} due to IR active vibrations ν_3 and ν_4.[22] The ionic $CF_3SO_3^-$ group has lower symmetry (C_{3v}), but the absence of splitting of the band at 1261 cm^{-1} (ν_3) is consistent with that character of OTf in **5**.[23] In the case of carboxylate derivatives it is generally accepted that it is possible to distinguish between ionic, unidentate, chelating bidentate, or bridging bidentate groups on the basis of the Δ values (where $\Delta = \nu_a(COO) - \nu_s(COO)$). In the spectrum of our tfa derivative **6** the Δ value is 182 cm^{-1} in accordance with an ionic formulation of this group.[24]

The chemical shifts of protons and carbons for the ligand in complexes **1**−**6** were similar to those of free ligands, only slightly shifted downfield compared with free ligands. These data indicate that extensive dissociation of **1**−**6** as suggested in eq 2 occurs in CD_3CN and DMSO-d_6, suggesting weaker interactions between the ligands and the silver(I) acceptors in these solvents.

The positive electrospray mass spectra of complexes **1**−**6** (the most relevant data are reported in the Experimental Section) indicate that these derivatives mainly undergo loss of the anionic X^- group. The isotopic distribution of these species is in accord with the calculated composition. Acetonitrile does show ligating properties itself toward silver(I) ions, and this is manifest in evidence for the formation of ions $[Ag(MeCN)]^+$, $[Ag(MeCN)_2]^+$, and $[Ag(MeCN)(tz_2(CH_2))]^+$. However, the aggregation behavior seems to be most strongly dependent on the counterion, the NO_3, tfa, and OTf groups being the more conspicuous coordinating anions in the vapor phase. Some small peaks present in the spectra of **1**, **5**, and **6** are due to the formation of bi- and trimetallic species $[Ag_2(tz_2(CH_2))_2(X)]^+$ and $[Ag_3(tz_2(CH_2))_2(X)_2]^+$ respectively. In the case of the OTf compound **5,** small peaks due to similar tetra- and pentametallic species were detected, as well, these ions containing bridging nitrito groups. The negative electrospray mass spectra are always dominated by the presence of molecular peaks due to X^-, $[AgCl(X)]^-$, $[Ag(X)_2]^-$, $[Ag_2(X)_3]^-$, and $[Ag_3(X)_4]^-$. No peaks containing the tz_2CH_2 ligand were found.

X-Ray Diffraction Studies: Discussion. Low-temperature single-crystal X-ray studies have defined the structures of the free ligand as well as its 1:1 adducts with silver(I) nitrate and nitrite, **1** and **2**, and the 3:4 adduct with AgOTf (as an acetonitrile solvate) **5**. In the free ligand, two-half molecules, each with a crystallographic 2-axis passing through the central carbon atom (Figure 1) make up the asymmetric unit of the structure, the geometries of the two independent molecules being in good agreement, and showing some enhancement of double bond localization in N(2)−C(3) and N(4)−C(5) (Table 1). The only other bis(1,2,4-triazol-1-yl)methane structure recorded, devoid of crystallographic symmetry, is aquadibromodiphenyltin(IV) bis(3,5-dimethyl-1,2,4-triazol-1-yl)methane,[15] in which the precision of the ligand geometry is inherently diminished by the rather high heavy atom content. Close intermolecular hydrogen contacts are found between H(15)···N(24) ($1/2 + x$, $1 - y$, $1/2 + z$), H(25)···N(14) ($1/2 - x$, $y - 1$, $1/2 - z$) 2.59(1), 2.62(1), as well as H(23)···N(12) ($1 - x$, $2 - y$, $\bar{z}$) 2.53(1) Å; within the complexes with silver(I), the interactions are predominantly by way of the N(4), so that the role of the ligand in

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(20) Addison, C. C.; Logan, N.; Wallwork, S. C.; Garner, C. D. *Q. Rev.* **1971**, *25*, 289−322. Lever, A. B. P.; Mantovani, E.; Ramaswamy, B. S. *Can. J. Chem.* **1971**, *49*, 1957−1964.

(21) Cornilsen, B. C.; Nakamoto, K. *J. Inorg. Nucl. Chem.* **1974**, *36*, 2467−2471. Goodgame, D. M. L.; Goodgame, M.; Hayward, P. J.; Rayner-Canham, G. W. *Inorg. Chem.* **1968**, *7*, 2447−2451.

(22) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331−335.

(23) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley & Sons: New York, 1986.

(24) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227−250.

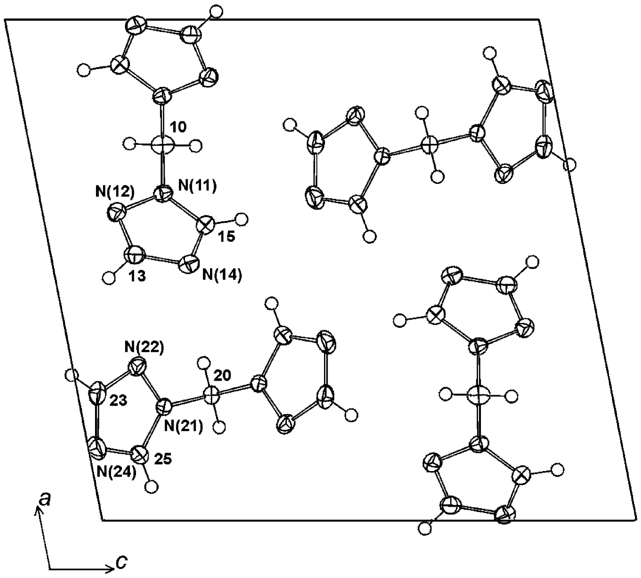

Figure 1. Unit cell contents of the free tz_2CH_2 ligand, projected down *b*.

Table 1. tz_2CH_2 Ligand Geometries[a]

	ligand	1:1 $AgNO_3$ adduct, **1**
	Distances, Å	
C(0)−N(1)	1.4458(8), 1.4483(7)	1.456(2), 1.446(2)
N(1)−N(2)	1.3640(8), 1.3627(9)	1.364(2), 1.368(2)
N(1)−C(5)	1.342(1), 1.3419(8)	1.336(2), 1.335(2)
N(2)−C(3)	1.322(1), 1.3215(9)	1.312(2), 1.318(3)
C(3)−N(4)	1.360(1), 1.364(1)	1.365(3), 1.362(2)
N(4)−C(5)	1.320(1), 1.326(1)	1.331(2), 1.324(2)
	Angles, deg	
N(1)−C(0)−N(1)	111.87(7), 111.52(6)	111.3(1)
C(0)−N(1)−N(2)	120.97(5), 121.12(4)	119.3(1), 122.1(1)
C(0)−N(1)−C(5)	129.07(5), 128.83(5)	129.6(2), 127.8(2)
N(2)−N(1)−C(5)	109.87(5), 110.05(5)	110.5(1), 110.0(1)
N(1)−N(2)−C(3)	101.99(6), 102.05(6)	102.9(1), 102.7(2)
N(2)−C(3)−N(4)	115.05(6), 115.18(7)	113.9(2), 113.9(2)
C(3)−N(4)−C(5)	102.81(6), 102.53(6)	104.0(2), 103.8(2)
N(1)−C(5)−N(4)	110.29(6), 110.20(6)	108.8(2), 109.6(2)
	C_2N_3/C_2N_3 Interplanar Dihedral Angle (θ, deg)	
θ	73.96(6), 75.67(6)	56.73(8)

[a] The geometry of the free ligand is compared with that of its most precisely determined present complex (the silver(I) nitrate adduct **1**). The two values in each entry are for molecules 1, 2 of the ligand, rings 1, 2 in the nitrate. In the ligand C,N−H distances are H(n0) 0.98(1), 0.97(1); H(n3) 1.00(1), 0.97(1); H(n5) 0.95(1), 0.92(1) Å. In **1**, N−O(1,2,3) are 1.256(3), 1.238(3), 1.250(3) Å, opposed angles being 120.1(2), 120.3(2), 119.7(2)°; the silver atoms lie 0.132(3), 0.524(3) Å out of the coordinating C_2N_3(tz) planes and 2.297(5), −1.300(6) Å to either side of the nitrate.

these complexes is primarily bridging, leading to polymers rather than chelates.

Although not isomorphous, silver(I) nitrite and nitrate adducts **1** and **2** crystallize in cells of very similar dimensionality. The roles of the anions in the two structures differ, almost all atoms of the nitrite anions interacting significantly with silver, whereas only one oxygen of the nitrate does so. Both structures, however, may be regarded as one-dimensional polymers or two-dimensional derivative thereof.

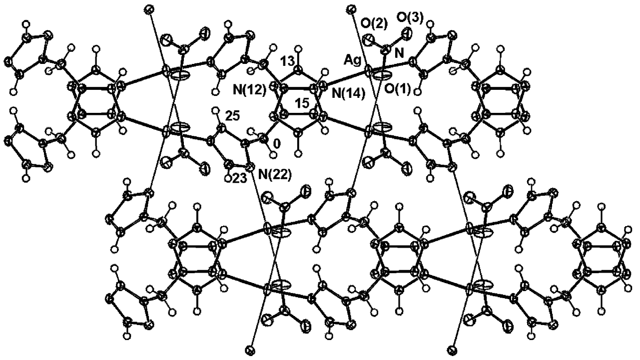

Figure 2. A section of the polymer of $AgNO_3$:tz_2CH_2 (1:1), **1**.

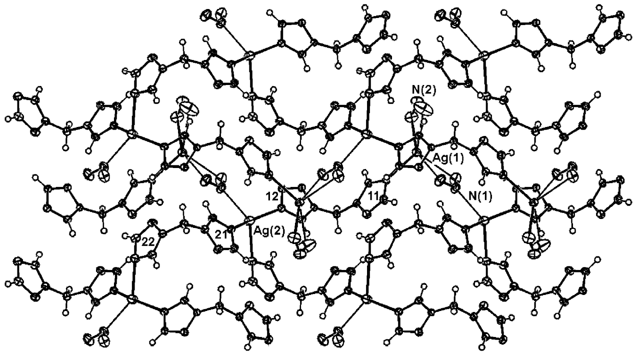

Figure 3. A section of the polymer of $AgNO_2$:tz_2CH_2 (1:1), **2**.

Table 2. Ag(1) Environment of the $AgNO_2$:tz_2CH_2 (1:1) Adduct, **2**[a]

atom	*r*, Å	O(11)	O(12)	O(21)	O(22)
N(14)	2.314(4)	89.1(2)	103.1(2)	116.6(2)	139.6(2)
O(11)	2.519(5)		47.6(2)	154.1(2)	113.4(1)
O(12)	2.670(5)			117.5(2)	116.9(2)
O(21)	2.420(5)				49.4(2)
O(22)	2.536(7)				

[a] *r* is the metal−ligand atom distance; other entries in the matrix are the angles (deg) subtended by the relevant atoms at the head of the row and column. N(1)−O(11,12), N(2)−O(11,12) are 1.237(6), 1.240(8), 1.253(6), 1.230(9) Å; O−N−O 115.8(5), 113.2(5) and N−O−Ag 102.0(4), 94.4(3), 101.3(4), 96.1(4)°. Ag(1) lies 0.22(1), 0.08(3) Å out of the NO_2 planes. C_2N_3/C_2N_3 interplanar dihedral angles for the two ligands are 64.8(2), 78.9(2)°; deviations (tz ring/silver atom) are 11/ 1 0.249(9), 12/2 0.385(8), 21/2 0.198(8), 22/2 (1 − *x*, *y* − 1/2, 2 − *z*) 1.552(8) Å. Ag(1)···Ag(2) (1 − *x*, 1/2 + *y*, 1 − *z*) is 3.4634(6) Å.

The structure of $AgNO_3$:L (1:1) **1** is shown in Figure 2; one formula unit, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure. The silver atom is essentially linearly coordinated by a pair of N(4) nitrogens from different rings of different ligands (Ag−N(14), N(24) (1/2 + *x*, 1/2 − *y*, 1 + *z*) 2.163(2), 2.164(2) Å; N−Ag−N 165.50(6)°), the succession of bridged components generated by the glide operation parallel to *c*. Polymer strands overlaid with juxtaposed silver atoms have the latter weakly bridged by only one of the nitrate oxygen atoms which interacts significantly: Ag−O(1),O(1) (1/ 2 + *x*, 1/2 − *y*, *z*) 2.645(2), 2.802(2) Å, further feeble cross-linking in the third dimension occurring through N(22) (Ag···N(22) (3/2 − *x*, 1/2 + *y*, 1/2 + *z*) 2.868(2) Å). Ag···Ag (1/2 + *x*, 1/2 − *y*, *z*) is 4.5110(3) Å.

The character of the silver(I) nitrite:tz_2CH_2 (1:1) adduct **2** is quite different, two formula units, again devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. The coordination of Ag(2) again is *quasi*-linear as in the nitrate, Ag(2)−N(124, 214) longer at 2.217(4), 2.194(4) Å, N−Ag−N concomitantly diminished to 151.0(2)°); perturbation of the coordination occurs through the agency of N(224) (1 − *x*, 1/2 + *y*, 2 − *z*) (2.499(4) Å)

Table 3. Coordination Environments AgOTf:tz$_2$CH$_2$ (3:4), **5**[a]

Ag(1)

atom	*r*	N(214)	N(312)	N(1121^{i})	N(122^{i})
N(114)	2.356(9)	96.8(3)	135.5(3)	127.2(3)	88.3(3)
N(214)	2.371(8)		100.5(3)	92.7(3)	169.6(3)
N(312)	2.385(8)			92.7(3)	81.9(3)
N(112^{i})	2.517(8)				77.1(3)
N(122^{i})	2.635(9)				

Ag(2)

atom	*r*	N(414)	N(212^{ii})	N(314^{iii})
N(124)	2.272(9)	107.1(3)	97.6(3)	119.7(3)
N(414)	2.301(9)		140.0(3)	99.7(3)
N(212^{ii})	2.371(8)			94.6(3)
N(314^{iii})	2.351(8)			

Ag(3)

atom	*r*	N(412^{iv})	N(422^{iv})	N(224^{ii})	N(424^{v})
N(324)	2.334(9)	97.1(3)	95.8(3)	121.3(3)	99.9(3)
N(412^{iv})	2.549(10)		75.7(3)	90.4(3)	159.6(3)
N(422^{iv})	2.705(10)			141.9(3)	91.4(3)
N(224^{ii})	2.317(9)				90.2(3)
N(424^{v})	2.390(10)				

[a] Interplanar dihedral angles within the ligands: 45.3(4), 72.1(4), 61.0(4), 73.4(5)°. Silver atom deviations from the C$_2$N$_3$ tz planes (plane/Ag) are 11/Ag(1), Ag(1^{vi}) 0.39(2), −0.74(2); 12/Ag(1^{vi},2) 0.99(2), −0.23(2); 21/Ag(1,2^{vii}) 0.36(2), 0.64(2); 22/Ag(3^{vii}) 0.27(2); 31/Ag(1,2^{viii}) 0.39(2), −0.01(2); 32/Ag(3) 0.20(2); 41/Ag(2,3^{ix}) 0.61(2), −0.84(2); 42/Ag(3^{ix,x}) 0.19(2), −0.29(2) Å. Transformations of the asymmetric unit: i, $1 - x$; $y - 1/2$, $3/2 - z$; ii x, $1 + y$, z; iii, $1 + x$, $1 + y$, z; iv, $x - 1$, y, z; v, $x - 1/2$, $3/2 - y$, $1 - z$; vi, $1 - x$, $1/2 + y$, $3/2 - z$; vii, x, $y - 1$, z; viii, $x - 1$, $y - 1$, z; ix, $1 + x$, y, z; x, $1/2 + x$, $3/2 - y$, $1 - z$.

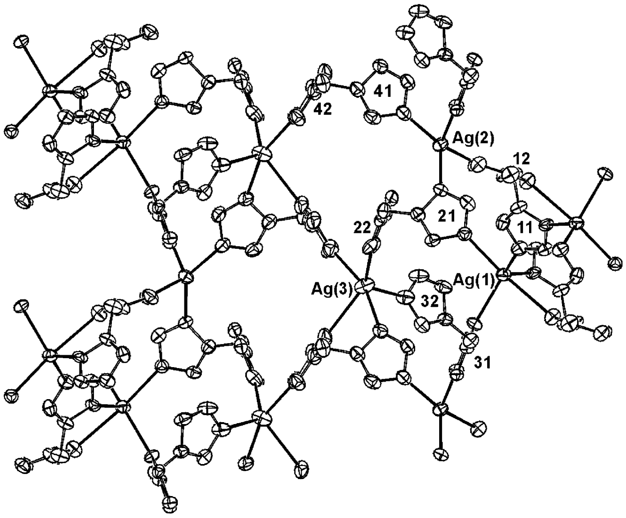

Figure 4. A section of the cationic (Ag$_3$L$_4$)$^{3+}$ polymer of AgOTf: tz$_2$CH$_2$ (3:4). MeCN, **5**.

and anion N(1) (x, $y - 1$, z) (2.572(5) Å) approaches. N(114) bridges to Ag(1) (2.315(4) Å) but the remainder of the coordination sphere of the latter is made up of a pair of *O*,*O*′-NO$_2$ chelates (Table 2), whereof N(1) bridge to Ag(2) as indicated above, forming a loose two-dimensional array woven about the 2$_1$ screw (Figure 3).

With a further diminution in anion basicity, it is unsurprising that the adduct obtained with silver(I) triflate is devoid of metal−anion interactions, with concomitant increase in salt:ligand stoichiometry; both anions and solvent are uncoordinated, occupying lattice sites. One AgOTf:L (3:4). MeCN formula unit, **5**, devoid of crystallographic symmetry, comprises the asymmetric unit of the structure, with the (Ag$_3$L$_4$)$^{3+}$ cationic array polymeric. The silver atom coordination environments are diverse; interestingly, the metal atom coordination spheres involve not only N(4) of each ligand ring (on a basis of one Ag per N donor) but also N(2) similarly (N(222, 322) excepted) (Table 3). Further, through the latter, ligands **1** and **4** behave as chelates, toward Ag(1, 3) respectively, with interplanar dihedral angles similar to those of the free ligand, except that their putative symmetry is now *m* rather than 2. A section of the polymer is shown in Figure 4.

Conclusion

In summary, we have synthesized a new series of silver(I)−tz$_2$CH$_2$ complexes, quite stable in the solid state, fully characterized by analytical and spectroscopic measurements. Solution data are consistent with complete dissociation of the complexes, occurring through breaking of Ag−N bonds. The ligand tz$_2$(CH$_2$) coordinates the silver atom through the nitrogen atoms yielding two- and three-dimensional coordination polymers. The replacement of the pyrazole rings in the familiar poly(pyrazolyl)alkanes by 1,2,4-triazole leads to a ligand which can bridge between metal centers, thereby creating coordination polymers with interesting solid-state structures and properties. The nature of the polymer is dependent on the counterions and independent of the ligand-to-metal ratio and reaction conditions employed.

Acknowledgment. We thank University of Camerino and CARIMA Foundation for financial help.

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

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