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Silver derivatives of tris(pyrazol-1-yl)methanes. A silver(I) nitrate complex containing a tris(pyrazolyl)methane coordinated in a bridging mode

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Abstract

The reaction of AgX (X = ClO₄, NO₃ or SO₃CH₃) acceptors with excesses of tris(pyrazol-1-yl)methane ligands L (L = CH(pz)₃, CH(4-Mepz)₃, CH(3,5-Me₂pz)₃, CH(3,4,5-Me₃pz)₃ or CH(3-Mepz)₂(5-Mepz)) yields 1:1 [AgX(L)], 2:1 [Ag(L)₂]X or 3:2 [(AgX)₂(L)₃] complexes. The ligand to metal ratio in all complexes is dependent on the number and disposition of the Me substituents on the azole ring of the neutral ligand and on the nature of the Ag(I) acceptor. All complexes have been characterized in the solid state as well as in solution (medium- and far-IR, ¹H and ¹³C NMR and conductivity determinations) and the solid-state structures of [Ag(NO₃){(pz)₃CH}]_(∞/∞) and [Ag{(3,5-Me₂pz)₃CH}]₂NO₃ determined by single crystal X-ray studies. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Silver complexes; Poly(pyrazolyl)alkanes complexes

1. Introduction

Since poly(pyrazol-1-yl)borate ligands were discovered and used by Trofimenko, their coordination chemistry has been extensively developed over the last few decades [1], with particular interest arising out of the ability of this class of ligands to modify or control the steric and electronic environment about the metal center by variation of the pyrazolyl groups.

Recently this group has focused on contrasting the chemistry of complexes of the neutral poly(pyrazol-1-yl)alkane ligands with that previously developed for anionic poly(pyrazol-1-yl)borates, in extension of which we have initiated a study of the coordination chemistry of neutral bis- and tris(pyrazol-1-yl)alkanes with several post-transition and transition metals [2]. While in the

last years numerous reports of poly(pyrazol-1-yl)borate–Ag(I) complexes have appeared [3], to date the chemistry of poly(pyrazol-1-yl)alkanes toward transition metals remains relatively unexplored.

In previous papers we have described interactions between Ag(I) and N₂-donors which have given a picture different from that obtained when other acceptors were employed [4]. In particular, strongly distorted tetrahedral complexes of general formula [(N₂-donor)₂Ag]X were obtained also when very weakly basic ligands, such as bis(4-nitropyrazol-1-yl)alkane, were used, possibly consequent on π-backdonation between a pyrazole nitrogen and silver [4], not found with Zn, Cd, Sn, Ni and Hg [2].

As an extension of this work, we now describe a study of the donor behavior of neutral, tris-chelating, flexible, stable N₃-donor tris(pyrazol-1-yl)methanes towards Ag(I) acceptors. With the aim of evaluating the importance of the substituents on the structure and properties of the concomitant Ag(I) complexes, we have prepared a series of ligands defined by the presence of

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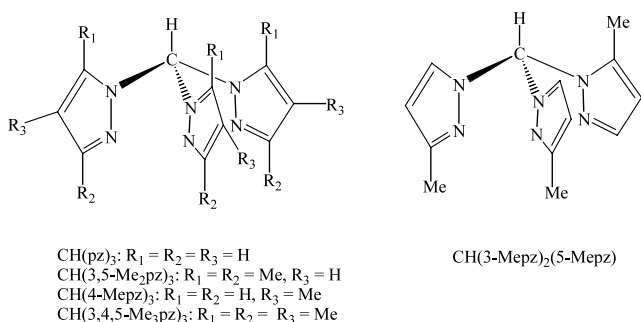


Fig. 1. Structures of the ligands employed in this work.

methyl groups in the 3-, 4- and 5-positions of the pyrazole ring $\text{CH}(\text{pz})_3$, $\text{CH}(4\text{-Mepz})_3$, $\text{CH}(3,5\text{-Me}_2\text{pz})_3$, $\text{CH}(3,4,5\text{-Me}_3\text{pz})_3$ or $\text{CH}(3\text{-Mepz})_2(5\text{-Mepz})$ (Fig. 1). We have shown that different reaction patterns may be found depending on the nature of the donor and of the Ag(I) acceptor. In order to gain insight into the factors controlling the structure and bonding in these complexes, and to synthesize complexes in which the same ligand may be coordinated to different metal centers, we have employed Ag(I) incorporating weakly donating oxyanions (ClO_4^- , NO_3^- and SO_3CH_3^-).

We report here the syntheses and properties of 15 new complexes. The solid-state structures for the derivatives $[\text{Ag}(\text{NO}_3)\{(\text{pz})_3\text{CH}\}]_{(\infty/\infty)}$, an infinite, unsolvated two-dimensional polymer containing a bridging tris(pyrazol-1-yl)methane ligand, and $[\text{Ag}\{(3,5\text{-Me}_2\text{pz})_3\text{CH}\}_2]\text{NO}_3$, have been determined by single crystal X-ray studies.

2. Experimental

2.1. Materials and methods

The Ag(I) salts were purchased from Aldrich (Milwaukee) and used as received. Solvent evaporations were carried out under vacuum with the use of a rotary evaporator. The samples for microanalysis were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). All syntheses were carried out under a nitrogen atmosphere. Hydrocarbon solvents were dried by distillation from sodium–potassium, dichloromethane from calcium hydride and tetrahydrofuran from sodium and benzophenone. All solvents were degassed with dry nitrogen prior to use.

Elemental analyses (C, H, N, S) were performed with a Fisons Instruments 1108 CHNSO Elemental analyzer. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer System 2000 FT–IR instrument. ^1H NMR spectra were recorded using a VXR-300 Varian spectrometer operating at room temperature (300 MHz for ^1H). ^{13}C NMR spectra were measured on a Bruker AC200 spectrometer operating at 50 MHz with a multi-

nuclear 10 mm probehead at room temperature. ^1H and ^{13}C NMR spectra chemical shifts are referred to the residual proton or carbon resonance of the deuterated solvents relative to TMS. Peaks multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; multiplet, m; pseudotriplet, pt; complex multiplet, mc; broad, br. Melting points are uncorrected and were taken on an IA 8100 Electrothermal instrument and on a capillary apparatus. The electrical conductance of the solutions was measured with a Crison CDTM 522 conductimeter at room temperature.

2.2. Syntheses

2.2.1. Syntheses of the ligands

2.2.1.1. Tris(pyrazol-1-yl)methane $\text{CH}(\text{pz})_3$. The ligand $\text{CH}(\text{pz})_3$ (44% yield) was obtained according to the published method [5]. ^1H NMR (CDCl_3): δ 6.37 (pt, 3H, 4-CH), 7.58 (d, 3H, 3- or 5-CH), 7.68 (d, 3H, 3- or 5-CH), 8.43 (s, 1H, CH). ^1H NMR (acetone- d_6): δ 6.40 (pt, 3H, 4-CH), 7.63 (d, 3H, 3- or 5-CH), 7.86 (d, 3H, 3- or 5-CH), 8.74 (s, 1H, CH). ^1H NMR (CD_3OD): δ 6.43 (t, 3H, 4-CH), 7.67 (d, 3H, 3- or 5-CH), 7.74 (d, 3H, 3- or 5-CH), 8.70 (s, 1H, CH). ^{13}C NMR (CDCl_3): δ 142.2 (3-C (pz)), 130.0 (5-C (pz)), 107.2 (4-C (pz)), 83.6 (CH). ^{13}C NMR ($\text{DMSO-}d_6$): δ 141.2 (3-C (pz)), 130.4 (5-C (pz)), 107.8 (4-C (pz)), 81.9 (CH).

2.2.1.2. Tris(3,5-dimethylpyrazol-1-yl)methane $\text{CH}(3,5\text{-Me}_2\text{pz})_3$. The ligand $\text{CH}(3,5\text{-Me}_2\text{pz})_3$ (42% yield) was obtained according to the published method [5]. ^1H NMR (CDCl_3): δ 2.01 (s, 9H, 3- or 5- CH_3), 2.18 (s, 9H, 3- or 5- CH_3), 5.88 (s, 3H, 4-CH), 8.09 (s, 1H, CH). ^{13}C NMR ($\text{DMSO-}d_6$): δ 147.3 (3-C (pz)), 140.2 (5-C (pz)), 107.4 (4-C (pz)), 80.0 (CH), 13.7, 10.6 (3- and 5- CH_3).

2.2.1.3. Tris(3,4,5-trimethylpyrazol-1-yl)methane $\text{CH}(3,4,5\text{-Me}_3\text{pz})_3$. The ligand $\text{CH}(3,4,5\text{-Me}_3\text{pz})_3$ (44% yield) was obtained according to the published method [6]. ^1H NMR (CDCl_3): δ 1.88 (s, 9H, 3- or 5- CH_3), 1.93 (s, 9H, 3- or 5- CH_3), 2.13 (s, 9H, 4- CH_3), 8.05 (s, 1H, CH). ^1H NMR (CD_3OD): δ 1.92 (s, 18H, 3- and 5- CH_3), 2.12 (s, 9H, 4- CH_3), 8.09 (s, 1H, CH). ^{13}C NMR (CDCl_3): δ 147.7 (3-C (pz)), 137.0 (5-C (pz)), 113.4 (4-C (pz)), 81.2 (CH), 12.4, 9.4, 8.1 (3-, 4- and 5- CH_3).

2.2.1.4. Tris(4-methylpyrazol-1-yl)methane $\text{CH}(4\text{-Mepz})_3$. The ligand $\text{CH}(4\text{-Mepz})_3$ (44% yield) was obtained according to the published method [6]. ^1H NMR (CDCl_3): δ 2.06 (s, 9H, 4- CH_3), 7.30 (s, 3H, 3- or 5-CH), 7.46 (s, 3H, 3- or 5-CH), 8.17 (s, 1H, CH). ^1H NMR (CD_3OD): δ 2.07 (s, 9H, 4- CH_3), 7.44 (s, 3H, 3- or 5-CH), 7.47 (s, 3H, 3- or 5-CH), 8.36 (s, 1H, CH). ^{13}C NMR (CDCl_3): δ 142.9 (3-C (pz)), 128.2 (5-C (pz)),

118.2 (4-*C* (pz)), 83.8 (CH), 9.4 (4-CH₃). ¹³C NMR (DMSO-*d*₆): δ 141.6 (3-*C* (pz)), 128.4 (5-*C* (pz)), 116.8 (4-*C* (pz)), 82.0 (CH), 8.8 (4-CH₃).

2.2.1.5. Bis(3-methylpyrazol-1-yl)(5-methylpyrazol-1-yl)methane CH(3-Mepz)₂(5-Mepz). The ligand CH(3-Mepz)₂(5-Mepz) (44% yield) was obtained according to the published method [6]. ¹H NMR (CDCl₃): δ 2.28 (s, 6H, 3-CH₃), 2.40 (s, 3H, 5-CH₃), 6.11 (d, 3H, 4-CH), 7.31 (d, 2H, 5-CH), 7.54 (d, 1H, 3-CH), 8.21 (s, 1H, CH). ¹³C NMR (CDCl₃): δ 150.7 (3-CCH₃ (pz)), 141.1 (3-*C* (pz)), 139.8 (5-CCH₃ (pz)), 129.7 (5-*C* (pz)), 107.1 (4-*C* (pz)), 80.4 (CH), 13.7, 10.8 (3- and 5-CH₃).

2.2.2. Synthesis of the complexes

2.2.2.1. [Ag{(pz)₃CH}CH₃OH]ClO₄ (1). To a stirred methanol solution (30 ml) of HC(pz)₃ (0.210 g, 0.981 mmol) at r.t., under nitrogen in a round-bottomed flask protected from the light, AgClO₄ (0.110 g, 0.53 mmol) was added. After approximately 12 h, the colorless precipitate formed was filtered off and washed with diethyl ether to give (27% yield) the analytical sample **1**. M.p.: 262–263 °C. ¹H NMR (CDCl₃): δ 3.5 (s, 3H, CH₃OH), 6.39 (pt, 3H, 4-CH), 7.68, 7.83 (2 d, 6H, 3- and 5-CH), 9.10 (s, 1H, CH). ¹H NMR (DMSO-*d*₆): δ 3.35 (s, 3H, CH₃OH), 6.46 (pt, 3H, 4-CH), 7.70, 8.00 (2 s, 6H, 3- and 5-CH), 9.09 (s, 1H, CH). ¹³C NMR (DMSO-*d*₆): δ 141.7, (3-CH), 131.0 (5-CH), 107.0 (4-CH), 80.6 (CH). Cond. (CH₂Cl₂, conc. = 1.01 × 10^{−3} M): *A* 0.45 Ω^{−1} cm² mol^{−1}. Anal. Found: C, 28.8; H, 2.9; N, 18.8. Calc. for C₁₁H₁₄AgClN₆O₅: C, 29.1; H, 3.1; N, 18.5%. IR (cm^{−1}): 3564 sbr [ν(O–H)], 3103 br, 3156 s, 3124 br, 3103 br [ν(C–H)], 1116 sbr, 1106 sbr, 1097 sbr, 1070 sbr, 642 s, 621 s, 610 sh [ν(ClO₄)].

2.2.2.2. [Ag(NO₃){(pz)₃CH}][H₂O] (2). Compound **2** (81% yield) was obtained similarly to compound **1** by using benzene as solvent. M.p.: 177–178 °C. ¹H NMR (CDCl₃): δ 1.63 (br, 2H, H₂O), 6.38 (pt, 3H, 4-CH), 7.67, 7.70 (2 d, 6H, 3- and 5-CH), 8.67 (s, 1H, CH). Cond. (CH₂Cl₂, conc. = 0.90 × 10^{−3} M): *A* 0.38 Ω^{−1} cm² mol^{−1}. Anal. Found: C, 30.1; H, 2.6; N, 24.0. Calc. for C₁₀H₁₂AgN₇O₄: C, 29.9; H, 3.0; N, 24.4%. IR (cm^{−1}): 3400 br [ν(H₂O)], 3106 br [ν(C–H)], 1398 sh, 1372 sbr, 720 s [ν(NO₃)]. Material for the diffraction study, devoid of water, was crystallized from benzene.

2.2.2.3. [Ag{(pz)₃CH}₂]SO₃CH₃·H₂O (3). To a stirred methanol solution (30 ml) of CH(pz)₃ (0.210 g, 0.981 mmol) at r.t., under nitrogen in a round-bottomed flask protected from the light, Ag(SO₃CH₃) (0.100 g, 0.493 mmol) was added. After approximately 12 h the solvent was removed with a rotary evaporator. To the residue was added diethyl ether (50 ml) and the reaction was carried out with stirring and at r.t. for 12 h; the

colorless precipitate formed was filtered off and washed with diethyl ether to give (72% yield) the analytical sample **3**. M.p.: 161–163 °C. ¹H NMR (CDCl₃): δ 1.9 (br, 2H, H₂O), 2.88 (s, 3H, SO₃–CH₃), 6.31 (pt, 6H, 4-CH), 7.59, 8.16 (2 d, 12H, 3- and 5-CH), 9.53 (s, 2H, CH). ¹³C NMR (CDCl₃): δ 142.6, (3-CH), 131.7 (5-CH), 107.3 (4-CH), 80.9 (CH), 39.5 (SO₃–CH₃). Cond. (CH₂Cl₂, conc. = 0.99 × 10^{−3} M): *A* 1.54 Ω^{−1} cm² mol^{−1}. Anal. Found: C, 38.5; H, 3.7; N, 25.1; S, 5.4. Calc. for C₂₁H₂₅AgN₁₂O₄S: C, 38.8; H, 3.9; N, 25.9; S, 4.9%. IR (cm^{−1}): 3400 br [ν(H₂O)], 3126 br, 3112 br, 3096 br [ν(C–H)].

2.2.2.4. [Ag{(3,5-Me₂pz)₃CH}₂]ClO₄ (4). To a stirred methanol solution (30 ml) of CH(3,5-Me₂pz)₃ (0.300 g, 1.005 mmol) at r.t., under nitrogen in a round-bottomed flask protected from the light, AgClO₄ (0.110 g, 0.531 mmol) was added. After approximately 12 h, the colorless precipitate formed was filtered off and washed with diethyl ether to give (98% yield) the analytical sample **4**. M.p.: 319 °C (dec.). ¹H NMR (CDCl₃): δ 1.89 (m, 18H, 3- or 5-CH₃), 2.39 (m, 18H, 3- or 5-CH₃), 5.91 (s, 6H, 4-CH), 7.92 (s, 2H, CH). ¹H NMR (DMSO-*d*₆): δ 1.85 (s, 18H, 3- or 5-CH₃), 2.36 (s, 18H, 3- or 5-CH₃), 5.90 (s, 6H, 4-CH), 8.01 (s, 2H, CH). ¹³C NMR (DMSO-*d*₆): δ 149.7 (3-CCH₃), 140.9 (5-CCH₃), 106.9 (4-CH), 71.8 (CH), 13.0, 10.3 (3- or 5-CH₃). Cond. (CH₂Cl₂, conc. = 1.09 × 10^{−3} M): *A* 51.1 Ω^{−1} cm² mol^{−1}. Anal. Found: C, 47.5; H, 5.7; N, 20.7. Calc. for C₃₂H₄₄AgClN₁₂O₄: C, 47.8; H, 5.5; N, 20.9%. IR (cm^{−1}): 3187 w, 3106 w, [ν(C–H)], 1090 sbr, 632 sh, 623 s [ν(ClO₄)].

2.2.2.5. [Ag{(3,5-Me₂pz)₃CH}₂][NO₃·H₂O] (5). Compound **5** (24% yield) was obtained similarly to compound **4**. M.p.: 299–300 °C. ¹H NMR (CDCl₃): δ 1.82 (br, 2H, H₂O), 1.93 (s, 18H, 3- or 5-CH₃), 2.41 (s, 18H, 3- or 5-CH₃), 5.90 (s, 6H, 4-CH), 7.98 (s, 2H, CH). ¹³C NMR (CDCl₃): δ 150.3 (3-CCH₃), 140.3 (5-CCH₃), 107.1 (4-CH), 72.2 (CH), 13.3, 10.8 (3- or 5-CH₃). Cond. (CH₂Cl₂, conc. = 0.99 × 10^{−3} M): *A* 36.0 Ω^{−1} cm² mol^{−1}. Anal. Found: C, 48.8; H, 6.0; N, 23.2. Calc. for C₃₂H₄₆AgN₁₃O₄: C, 49.0; H, 5.9; N, 23.2%. IR (cm^{−1}): 3200 br [ν(H₂O)], 3128 w, 3094 w [ν(C–H)], 1316 sbr, 720 s [ν(NO₃)].

2.2.2.6. [Ag{(3,5-Me₂pz)₃CH}₂]SO₃CH₃ (6). Compound **6** (91% yield) was obtained similarly to compound **3**, using CH(3,5-Me₂pz)₃ as ligand. M.p.: 270–271 °C. ¹H NMR (CDCl₃): δ 1.90 (s, 18H, 3- or 5-CH₃), 2.43 (s, 18H, 3- or 5-CH₃), 2.76 (s, 3H, SO₃–CH₃), 5.89 (s, 6H, 4-CH), 7.93 (s, 2H, CH). ¹³C NMR (CDCl₃): δ 150.5, (3-CCH₃), 140.1 (5-CCH₃), 107.1 (4-CH), 71.3 (CH), 39.4 (SO₃–CH₃), 13.3, 11.0 (3- or 5-CH₃). Cond. (CH₂Cl₂, conc. = 1.03 × 10^{−3} M): *A* 50.7 Ω^{−1} cm² mol^{−1}. Anal. Found: C, 49.3; H, 6.1; N, 20.6; S, 4.0.

Calc. for $C_{33}H_{47}AgN_{12}O_3S$: C, 49.6; H, 5.9; N, 21.0; S, 4.0%. IR (cm^{-1}): 3189 w, 3125 w, $[\nu(C-H)]$.

2.2.2.7. $[Ag\{(3,4,5-Me_3pz)_3CH\}_2]ClO_4$ (**7**). Compound **7** (74% yield) was obtained similarly to compound **4** using $HC(3,4,5-Me_3pz)_3$ as ligand. M.p.: 296 °C (dec.). 1H NMR ($CDCl_3$): δ 1.79 (s, 18H, 3- or 5- CH_3), 1.86 (s, 18H, 3- or 5- CH_3), 2.35 (s, 18H, 4- CH_3), 7.92 (s, 2H, CH). ^{13}C NMR ($CDCl_3$): δ 149.5, (3- CCH_3), 136.4 (5- CCH_3), 113.3 (4- CCH_3), 71.7 (CH), 11.5, 9.5, 7.8 (3- or 4- or 5- CH_3). Cond. (CH_2Cl_2 , conc. = 0.99×10^{-3} M): Λ 47.9 $\Omega^{-1} cm^2 mol^{-1}$. Anal. Found: C, 51.2; H, 6.7; N, 18.9. Calc. for $C_{38}H_{56}AgClN_{12}O_4$: C, 51.4; H, 6.4; N, 18.9. IR (cm^{-1}): 3158 w $[\nu(C-H)]$, 1081 sbr, 624 s $[\nu(ClO_4)]$.

2.2.2.8. $[(AgNO_3)_2\{(3,4,5-Me_3pz)_3CH\}_3]$ (**8**). To a stirred methanol solution (30 ml) of $CH(3,4,5-Me_2pz)_3$ (0.340 g, 1.00 mmol) at r.t., under nitrogen in a round-bottomed flask protected from the light, $AgNO_3$ (0.085 g, 0.500 mmol) was added. After approximately 12 h the solvent was removed with a rotary evaporator. To the residue diethyl ether (50 ml) was added and the reaction was carried out with stirring at r.t. for 12 h; the colorless precipitate formed was filtered off and washed with diethyl ether to give (72% yield) the analytical sample **8**. M.p.: 205 °C (dec.). 1H NMR ($CDCl_3$): δ 1.86 (s, 27H, 3- or 5- CH_3), 2.06 (s, 27H, 3- or 5- CH_3), 2.35 (s, 27H, 4- CH_3), 7.85 (s, 3H, CH). ^{13}C NMR ($CDCl_3$): δ 150.1 (3- CCH_3), 136.3 (5- CCH_3), 113.5 (4- CCH_3), 70.8 (CH), 12.2, 9.5, 7.8 (3- or 4- or 5- CH_3). Cond. (CH_2Cl_2 , conc. = 1.06×10^{-3} M): Λ 13.1 $\Omega^{-1} cm^2 mol^{-1}$. Anal. Found: C, 49.9; H, 6.1; N, 20.2. Calc. for $C_{57}H_{84}Ag_2N_{20}O_6$: C, 50.3; H, 6.2; N, 20.6%. IR (cm^{-1}): 3144 w $[\nu(C-H)]$, 1320 sbr, 1310 s, 729 s $[\nu(NO_3)]$.

2.2.2.9. $[(AgSO_3CH_3)_2\{(3,4,5-Me_3pz)_3CH\}_3]$ (**9**). Compound **9** (95% yield) was obtained similarly to compound **8**. M.p.: 146 °C (dec.). 1H NMR ($CDCl_3$): δ 1.86 (s, 54H, 3- and 5- CH_3), 2.34 (s, 27H, 4- CH_3), 2.82 (s, 6H, SO_3-CH_3), 7.89 (s, 3H, CH). Cond. (CH_2Cl_2 , conc. = 1.17×10^{-3} M): Λ 47.7 $\Omega^{-1} cm^2 mol^{-1}$. Anal. Found: C, 50.2; H, 6.7; N, 17.7; S, 4.2. Calc. for $C_{59}H_{90}Ag_2N_{18}O_6S_2$: C, 49.6; H, 6.4; N, 17.7; S, 4.5%. IR (cm^{-1}): 3098 w $[\nu(C-H)]$.

2.2.2.10. $[AgClO_4(4-Mepz)_3CH]$ (**10**). Compound **10** (35% yield) was obtained similarly to compound **1** using $CH(4-Mepz)_3$ as ligand. M.p.: 203 °C (dec.). 1H NMR ($CDCl_3$): δ 2.02 (s, 9H, 4- CH_3), 7.41 (s, 3H, 3- or 5-CH), 7.77 (s, 3H, 3- or 5-CH), 8.76 (s, 1H, CH). 1H NMR (CD_3OD): δ 2.07 (s, 9H, 4- CH_3), 7.53 (s, 3H, 3- or 5-CH), 7.79 (s, 3H, 3- or 5-CH), 8.78 (s, 1H, CH). 1H NMR ($DMSO-d_6$): δ 2.00 (s, 9H, 4- CH_3), 7.47 (s,

3H, 3- or 5-CH), 7.65 (s, 3H, 3- or 5-CH), 8.71 (s, 1H, CH). ^{13}C NMR ($DMSO-d_6$): δ 141.8 (3-CH), 128.6 (5-CH), 116.6 (4- CCH_3), 81.1 (CH), 8.5 (4- CCH_3). Cond. (CH_2Cl_2 , conc. = 1.06×10^{-3} M): Λ 2.72 $\Omega^{-1} cm^2 mol^{-1}$. Anal. Found: C, 34.0; H, 3.6; N, 18.1. Calc. for $C_{13}H_{16}AgClN_6O_4$: C, 33.7; H, 3.5; N, 18.1%. IR (cm^{-1}): 3149 br, 3113 s $[\nu(C-H)]$, 1130 sh, 1098 sbr, 1076 sbr, 624 s, 604 s $[\nu(ClO_4)]$.

2.2.2.11. $[(AgNO_3)_2\{(4-Mepz)_3CH\}_3] \cdot (H_2O)$ (**11**). Compound **11** (69% yield) was obtained similarly to compound **8** using $CH(4-Mepz)_3$ as ligand. M.p.: 118–119 °C. 1H NMR ($CDCl_3$): δ 1.68 (br, 2H, H_2O), 2.01 (s, 27H, 4- CH_3), 7.40 (s, 9H, 3- or 5-CH), 7.74 (s, 9H, 3- or 5-CH), 9.19 (s, 3H, CH). Cond. (CH_2Cl_2 , conc. = 1.01×10^{-3} M): Λ 2.76 $\Omega^{-1} cm^2 mol^{-1}$. Anal. Found: C, 41.4; H, 4.6; N, 24.6. Calc. for $C_{39}H_{50}Ag_2N_{20}O_7$: C, 41.6; H, 4.5; N, 24.9%. IR (cm^{-1}): 3412 br $[\nu(H_2O)]$, 3078 br $[\nu(C-H)]$, 1360 sbr, 722 s $[\nu(NO_3)]$.

2.2.2.12. $[(AgSO_3CH_3)_2\{(4-Mepz)_3CH\}_3] \cdot (H_2O)_2$ (**12**). Compound **12** (33% yield) was obtained similarly to compound **3** using $CH(4-Mepz)_3$ as ligand. M.p.: 118 °C (dec.). 1H NMR ($CDCl_3$): δ 1.66 (br, 4H, H_2O), 1.99 (s, 27H, 4- CH_3), 2.92 (s, 6H, SO_3-CH_3), 7.38 (s, 9H, 3- or 5-CH), 7.87 (s, 9H, 3- or 5-CH), 9.26 (s, 3H, CH). ^{13}C NMR ($CDCl_3$): δ 143.4 (3-CH), 130.5 (5-CH), 117.6 (4- CCH_3), 80.0 (CH), 39.4 (SO_3-CH_3), 8.7 (4- CCH_3). Cond. (CH_2Cl_2 , conc. = 0.86×10^{-3} M): Λ 3.02 $\Omega^{-1} cm^2 mol^{-1}$. Anal. Found: C, 40.4; H, 4.8; N, 20.6; S, 5.5. Calc. for $C_{41}H_{58}Ag_2N_{18}O_8S_2$: C, 40.7; H, 4.8; N, 20.8; S, 5.3%. IR (cm^{-1}): 3400 br $[\nu(H_2O)]$, 3093 br $[\nu(C-H)]$.

2.2.2.13. $[Ag\{(3-Mepz)_2(5-Mepz)CH\}_2]ClO_4$ (**13**). Compound **13** (67% yield) was obtained similarly to compound **1** using $HC(3-Mepz)_2(5-Mepz)$ as ligand. M.p.: 269–271 °C. 1H NMR ($CDCl_3$): δ 2.12 (s, 12H, 3- CH_3), 2.37 (s, 6H, 5- CH_3), 6.12 (br, 6H, 4-CH), 7.55 (s, 2H, 3-CH), 7.93 (s, 4H, 5-CH), 8.64 (s, 2H, CH). ^{13}C NMR ($CDCl_3$): δ 152.2 (3- CCH_3 (pz)), 142.1 (3-C (pz)), 141.8 (5- CCH_3 (pz)), 133.3 (5-C (pz)), 107.4 (4-C (pz)), 77.7 (CH), 14.4, 11.5 (3- and 5- CH_3). Cond. (CH_2Cl_2 , conc. = 0.94×10^{-3} M): Λ 12.16 $\Omega^{-1} cm^2 mol^{-1}$. Anal. Found: C, 43.1; H, 4.6; N, 23.2. Calc. for $C_{26}H_{32}AgClN_{12}O_4$: C, 43.4; H, 4.5; N, 23.3%. IR (cm^{-1}): 3142 br, 3122 s $[\nu(C-H)]$, 1094 sbr, 1056 sbr, 622 s $[\nu(ClO_4)]$.

2.2.2.14. $[(AgNO_3)_2(3-Mepz)_2(5-Mepz)CH\}_3] \cdot H_2O$ (**14**). Compound **14** (75% yield) was obtained similarly to compound **8** using $CH(3-Mepz)_2(5-Mepz)$ as ligand. M.p.: 241 °C (dec.). 1H NMR ($CDCl_3$): δ 1.65 (br, 2H, H_2O), 2.15 (s, 18H, 3- CH_3), 2.46 (s, 9H, 5- CH_3), 6.10 (s, 9H, 4-CH), 7.55 (s, 3H, 3-CH), 8.10 (s, 6H, 5-CH),

Table 1
The silver environments^a

(a) $[Ag(NO_3)(pz)_3CH] (1:1)_{2(\infty/\infty)}$ ^b						
Ag(1)	<i>r</i>	N(212)	O(11)	O(21)	O(23)	
N(112)	2.24(1)	121.5(4)	125.1(5)	107.8(3)	89.5(4)	
N(212)	2.28(1)		93.4(4)	117.0(3)	95.8(7)	
O(11)	2.38(1)			87.4(4)	130.8(5)	
O(21)	2.506(9)				45.9(3)	
O(23)	2.90(1)					
Ag(2)	<i>r</i>	N(132 ⁱ)	N(222 ⁱⁱ)	N(232 ⁱⁱ)	O(21)	O(22)
N(122 ⁱ)	2.32(1)	75.9(3)	114.4(4)	157.3(3)	85.0(3)	103.1(3)
N(132 ⁱ)	2.59(1)		114.5(3)	82.5(3)	152.6(3)	120.2(3)
N(222 ⁱⁱ)	2.38(1)			80.9(4)	91.1(3)	119.1(4)
N(232 ⁱⁱ)	2.38(1)				112.5(3)	81.6(3)
O(21)	2.738(9)					45.4(3)
O(22)	2.82(1)					
(b) $[Ag\{(3,5-Me_2pz)_2CH\}_2]NO_3 \cdot H_2O (1:2)$ ^c						
Primed atoms are related by the inversion center at the silver atom.						
Atom	<i>r</i>	N(22)	N(32)	N(21')	N(22')	N(32')
N(12)	2.434(1)	75.25(4)	74.96(4)	180(—)	104.75(4)	105.04(4)
N(22)	2.455(1)		79.00(4)	(104.75(4))	180(—)	101.00(4)
N(32)	2.594(1)			(105.04(4))	(101.00(4))	180(—)

^a *r* (Å) are the silver–ligand atom distances, other entries being the angles (°) subtended by the relevant atoms at the head of the row and column of the matrix. θ_{lm} (°) are the interplanar dihedral angles between the pyrazolate planes.

^b i, ii are the transformations $x, y, z-1$; $x-1, y, z$. $\theta_{11/12,13}$, $\theta_{12/13}$ are 65.8(6), 50.1(6), 64.6(6); $\theta_{21/22,23}$, $\theta_{22/23}$ are 55.1(6), 77.3(6), 47.6(6)°, respectively. Associated Ag deviations are (planes 11–13; 21–23) 0.27(2) (Ag(1)), 0.93(6) (Ag(2)), 1.69 (Ag(2ⁱⁱ); 0.03(2) Ag(1), 1.20(2) (Ag(2ⁱⁱ)), 0.61(2) Å (Ag(2ⁱⁱ)). Ag deviations from NO₃ planes 1,2 are: 1.07(3) (Ag(1)), 0.27(3), 0.52(9) (Ag(2^{i,ii})); 0.31(2) (Ag(1)), 0.10(2) (Ag(2)).

^c $\theta_{1/2,3}$ are 67.24(5), 74.44(5); $\theta_{2/3}$ is 85.34(5)°; $\delta Ag(C_5N_2$ planes 1,2,3) are 1.456(2), 1.148(2), 2.005(2) Å.

9.06 (s, 3H, CH). ¹³C NMR (CDCl₃): δ 151.8 (3-CCH₃ (pz)), 141.7 (3-C (pz)), 141.3 (5-CCH₃ (pz)), 133.1 (5-C (pz)), 106.9, 106.8 (4-C (pz)), 76.7 (CH), 13.4, 10.8 (3- and 5-CH₃). Cond. (CH₂Cl₂, conc. = 0.86×10^{-3} M): Λ 8.66 Ω^{-1} cm² mol⁻¹. Anal. Found: C, 41.4; H, 4.6; N, 24.6. Calc. for C₃₉H₅₀Ag₂N₂₀O₇: C, 41.6; H, 4.5; N, 24.9%. IR (cm⁻¹): 3400 br [ν (H₂O)], 3126 w, 3102 br [ν (C–H)], 1317 sbr, 768 s [ν (NO₃)].

2.2.2.15. $[Ag\{(3-Mepz)_2(5-Mepz)CH\}_2]SO_3CH_3 \cdot H_2O$ (**15**). Compound **15** (50% yield) was obtained similarly to compound **3** using HC(3-Mepz)₂(5-Mepz) as ligand. M.p.: 249 °C (dec.). ¹H NMR (CDCl₃): δ 1.8 (br, 2H, H₂O), 2.14 (s, 12H, 3-CH₃), 2.44 (s, 6H, 5-CH₃), 2.87 (s, 3H, Ag–CH₃), 6.10 (s, 6H, 4-CH), 7.55 (s, 2H, 3-CH), 8.11 (s, 4H, 5-CH), 9.00 (s, 2H, CH). ¹³C NMR (CDCl₃): δ 151.4 (3-CCH₃ (pz)), 141.4 (3-C (pz)), 141.2 (5-CCH₃ (pz)), 132.9 (5-C (pz)), 106.9, 106.7 (4-C (pz)), 77.2 (CH), 39.7 (SO₃–CH₃), 13.9, 11.1 (3- and 5-CH₃). Cond. (CH₂Cl₂, conc. = 1.09×10^{-3} M): Λ 3.17 Ω^{-1} cm² mol⁻¹. Anal. Found: C, 43.8; H, 5.1; N, 22.6; S, 4.6. Calc. for C₂₇H₃₇AgN₁₂O₄S: C, 44.2; H, 5.1; N, 22.9; S, 4.4%. IR (cm⁻¹): 3450 br [ν (H₂O)], 3127 w, 3100 m [ν (C–H)].

2.3. Structure determinations

For $[Ag(NO_3)\{(pz)_3CH\}]_{(\infty/\infty)}$, a unique single counter data set was measured (*T* ca. 295 K; $2\theta_{\max} = 50^\circ$) yielding *N* = 4653 independent reflections, *N*_o = 2253 with *I* > 3σ(*I*) being considered ‘observed’, gaussian absorption correction being applied. For $[Ag\{(3,5-Me_2pz)_2CH\}_2]NO_3 \cdot H_2O$, a full sphere of CCD area detector data was measured (*T* ca. 153 K; ω -scans, $2\theta_{\max} = 58^\circ$), 20 897 reflections merging to *N* = 4581 (*R*_{int} = 0.022) after ‘empirical’/multiscan absorption correction, *N*_o (*F* > 4σ(*F*)) = 3757. Anisotropic thermal parameter forms were refined for the non-hydrogen atoms, conventional residuals *R*, *R*_w (statistical weights) on |*F*| being quoted. Pertinent results are given in Table 1 and Figs. 4–5, the latter showing 20 (*T* ca. 295 K), 50% (*T* ca. 153 K) displacement amplitudes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

2.4. Crystal/refinement data

2.4.1. $[Ag(NO_3)\{(pz)_3CH\}]_{(\infty/\infty)}$ (**2**)

C₁₀H₁₀AgN₇O₃, *M* = 384.1. Monoclinic, space group *P*2₁/*n* (*C*_{2h}, No. 14, variant), *a* = 8.842(5), *b* = 30.42(1),

$c = 9.895(4) \text{ \AA}$, $\beta = 96.14(4)^\circ$. $V = 2646 \text{ \AA}^3$. D_{calc} ($Z = 8$) = 1.92_8 g cm^{-3} . $\mu_{\text{Mo}} = 15.5 \text{ cm}^{-1}$; specimen: $0.09 \times 0.04 \times 0.46 \text{ mm}$. $\langle T \rangle_{\text{min,max}} = 0.89, 0.94$. $R = 0.057$, $R_w = 0.053$. $|\Delta\rho_{\text{max}}| = 1.85(4) \text{ e \AA}^{-3}$. ($x, y, z, U_{\text{iso}}\text{H}$) included, constrained at estimated values.

2.4.2. $[Ag\{(3,5\text{-Me}_2\text{pz})_3\text{CH}\}_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ (**5**)

$\text{C}_{32}\text{H}_{46}\text{AgN}_{13}\text{O}_{14}$, $M = 784.7$. Monoclinic, space group $P2_1/c$ (C_{2h}^5 , No. 14), $a = 8.9162(8)$, $b = 12.498(1)$, $c = 16.221(2) \text{ \AA}$, $\beta = 92.321(1)^\circ$. $V = 1806 \text{ \AA}^3$. D_{calc} ($Z = 2$) = 1.44_3 g cm^{-3} . $\mu_{\text{Mo}} = 6.1 \text{ cm}^{-1}$; specimen: $0.16 \times 0.14 \times 0.10 \text{ mm}$. $\langle T \rangle_{\text{min,max}} = 0.80, 0.89$. $R = 0.025$, $R_w = 0.033$. $|\Delta\rho_{\text{max}}| = 0.57(3) \text{ e \AA}^{-3}$. ($x, y, z, U_{\text{iso}}\text{H}$) refined (H_2O excepted).

In the latter compound, as modeled in space group $P2_1/c$, the nitrate was modeled as disordered about a center of symmetry, its disorder concerted with that of

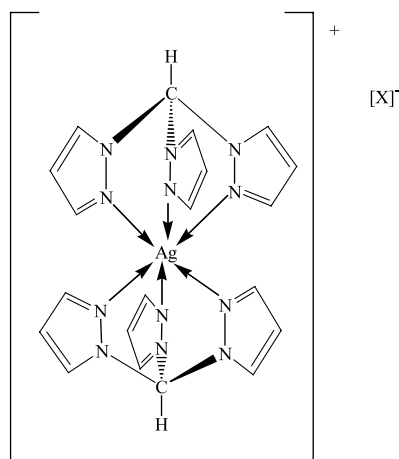


Fig. 2. The octahedral environment for the ionic 2:1 complexes.

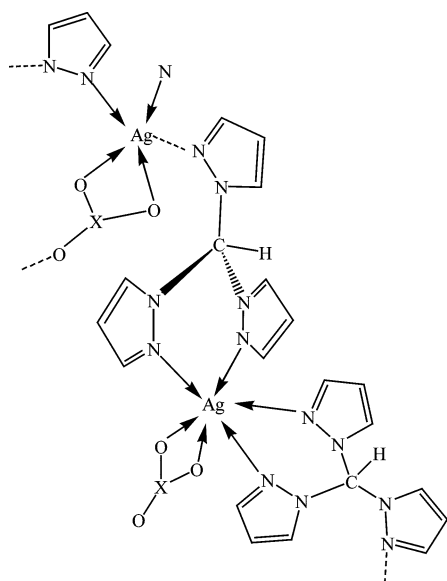


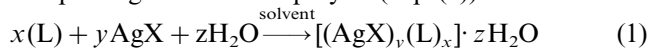
Fig. 3. Polynuclear motif possible for the 1:1 and 3:2 complexes.

a companion water molecule at the symmetry related site. Available specimens were rather small, the present CCD determination being preceded by an inferior room temperature study with data from a single counter instrument, no non-trivial differences being found between the two studies. At approximately 295 K, $a = 8.962(2)$, $b = 12.819(3)$, $c = 16.191(3) \text{ \AA}$, $\beta = 92.59(2)^\circ$, $V = 1858 \text{ \AA}^3$, $D_{\text{calc}} = 1.37_0 \text{ g cm}^{-3}$.

3. Results and discussion

3.1. Syntheses and properties

The interaction between Ag(I) acceptors AgX ($X = \text{ClO}_4$, NO_3 or CH_3SO_3) and $\text{CH}(\text{pz})_3$, $\text{CH}(4\text{-Mepz})_3$, $\text{CH}(3,5\text{-Me}_2\text{pz})_3$, $\text{CH}(3,4,5\text{-Me}_3\text{pz})_3$ or $\text{CH}(3\text{-Mepz})_2(5\text{-Mepz})$ in methanol or benzene always resulted in compounds **1–15** independently of reaction conditions and acceptor:ligand ratio employed (Eq. (1)).



- | | | | | |
|-----------|---|---------|---------|---------|
| 1 | $\text{L} = \text{HC}(\text{pz})_3$
$\text{X} = \text{ClO}_4$ | $x = 1$ | $y = 1$ | $z = 0$ |
| 2 | $\text{L} = \text{HC}(\text{pz})_3$
$\text{X} = \text{NO}_3$ | $x = 1$ | $y = 1$ | $z = 1$ |
| 3 | $\text{L} = \text{HC}(\text{pz})_3$
$\text{X} = \text{SO}_3\text{CH}_3$ | $x = 2$ | $y = 1$ | $z = 1$ |
| 4 | $\text{L} = \text{HC}(3,5\text{-Me}_2\text{pz})_3$
$\text{X} = \text{ClO}_4$ | $x = 2$ | $y = 1$ | $z = 0$ |
| 5 | $\text{L} = \text{HC}(3,5\text{-Me}_2\text{pz})_3$
$\text{X} = \text{NO}_3$ | $x = 2$ | $y = 1$ | $z = 1$ |
| 6 | $\text{L} = \text{HC}(3,5\text{-Me}_2\text{pz})_3$
$\text{X} = \text{SO}_3\text{CH}_3$ | $x = 2$ | $y = 1$ | $z = 0$ |
| 7 | $\text{L} = \text{HC}(3,4,5\text{-Me}_3\text{pz})_3$
$\text{X} = \text{ClO}_4$ | $x = 2$ | $y = 1$ | $z = 0$ |
| 8 | $\text{L} = \text{HC}(3,4,5\text{-Me}_3\text{pz})_3$
$\text{X} = \text{NO}_3$ | $x = 3$ | $y = 2$ | $z = 0$ |
| 9 | $\text{L} = \text{HC}(3,4,5\text{-Me}_3\text{pz})_3$
$\text{X} = \text{SO}_3\text{CH}_3$ | $x = 3$ | $y = 2$ | $z = 0$ |
| 10 | $\text{L} = \text{HC}(4\text{-Mepz})_3$
$\text{X} = \text{ClO}_4$ | $x = 1$ | $y = 1$ | $z = 0$ |
| 11 | $\text{L} = \text{HC}(4\text{-Mepz})_3$
$\text{X} = \text{NO}_3$ | $x = 3$ | $y = 2$ | $z = 1$ |
| 12 | $\text{L} = \text{HC}(4\text{-Mepz})_3$
$\text{X} = \text{SO}_3\text{CH}_3$ | $x = 3$ | $y = 2$ | $z = 2$ |
| 13 | $\text{L} = \text{HC}(3\text{-Mepz})_2(5\text{-Mepz})$
$\text{X} = \text{ClO}_4$ | $x = 2$ | $y = 1$ | $z = 0$ |
| 14 | $\text{L} = \text{HC}(3\text{-Mepz})_2(5\text{-Mepz})$
$\text{X} = \text{NO}_3$ | $x = 3$ | $y = 2$ | $z = 1$ |
| 15 | $\text{L} = \text{HC}(3\text{-Mepz})_2(5\text{-Mepz})$
$\text{X} = \text{SO}_3\text{CH}_3$ | $x = 2$ | $y = 1$ | $z = 1$ |

The analytical and spectral data of the tris(pyrazolyl)methane ligands and their complexes **1–15** are listed in Section 2.

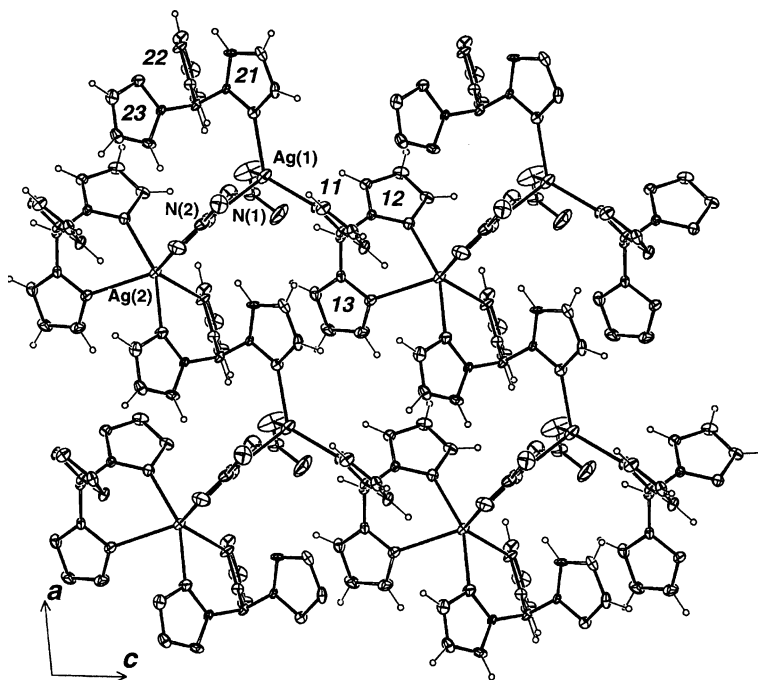


Fig. 4. The two-dimensional web of $[\text{Ag}(\text{NO}_3)(\text{pz})_3\text{CH}]$ (1:1) $_{2(\infty|\infty)}$ projected down b .

All complexes **1–15** are colorless solids and their stabilities in air and at room temperature differ depending on the nature of the ligand and of the counterion. All derivatives, when exposed to atmosphere decompose yielding metallic silver. The derivatives of AgNO_3 decompose rapidly; those containing the $\text{HC}(3,5\text{-Me}_2\text{pz})_3$ and $\text{HC}(3,4,5\text{-Me}_3\text{pz})_3$ ligands are the most stable.

All the complexes show good solubility in methanol, chlorinated solvents and acetone, exceptions being found in derivatives **1**, **2** and **10**, which are poorly soluble in chlorinated solvents, probably due to their poly- or oligomeric nature (see below). They are stable in CH_2Cl_2 or methanol, whereas in chloroform solutions they slowly decompose with deposition of $\text{Ag}(0)$. An exception is represented by the complex $[\text{Ag}(\text{NO}_3)\{(\text{pz})_3\text{CH}\}]\cdot\text{H}_2\text{O}$ (**2**), which readily decomposes in methanol solution, in a nitrogen atmosphere and in the dark; in fact derivative **2** has been obtained only using benzene as reaction solvent.

The compounds **1–15** display 1:1 (**1**, **2** and **10**), 2:1 (**3–7**, **13** and **15**) and 3:2 (**8**, **9**, **11**, **12** and **14**) ligand to metal ratios. The stoichiometries of the final products are influenced by the nature of the counterion and by the number and the location of methyl groups in the pyrazole rings of the ligands independently of the acceptor:ligand ratio used, the greater ligand to metal ratio being found when the more basic donors such as $\text{CH}(3,5\text{-Me}_2\text{pz})_3$ or $\text{CH}(3,4,5\text{-Me}_3\text{pz})_3$ or the less coordinating anions such as ClO_4 or SO_3CH_3 were employed. The complexes **3–7**, **13** and **15**, for which a 2:1 ligand to metal ratio has been found, likely have a

mononuclear structure as that in Fig. 2, as also confirmed by the X-ray single crystal study of **5**, whereas a poly- or oligonuclear structure with bridging tris(pyrazol-1-yl)methane and/or weakly coordinating anions, as in the structure of **2** (see below), appears probable for compounds **1**, **2**, **8–12**, and **14** (Fig. 3).

Conductivity measurements (see Section 2) were carried out in CH_2Cl_2 for all the derivatives **1–15**. The derivatives of $\text{CH}(\text{pz})_3$ and $\text{CH}(4\text{-Mepz})_3$ are non-electrolytes in CH_2Cl_2 whereas those of $\text{CH}(3,5\text{-Me}_2\text{pz})_3$ and $\text{CH}(3,4,5\text{-Me}_3\text{pz})_3$, the most basic and the most sterically hindered ligands, exhibit conductivity values in CH_2Cl_2 typical of a 1:1 electrolyte. Finally the

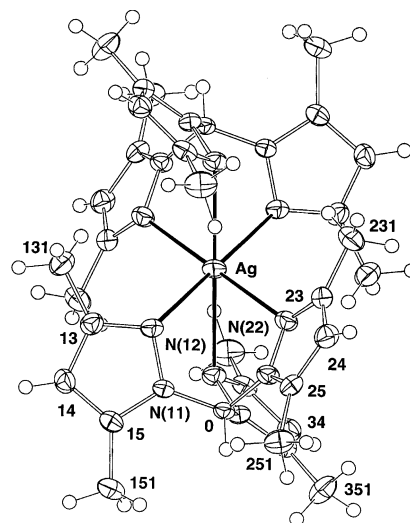
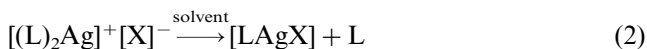


Fig. 5. The $[\text{Ag}\{(\text{3,5-Me}_2\text{pz})_3\text{CH}\}_2]^+$ cation.

derivatives of $\text{CH}(3\text{-Mepz})_2(5\text{-Mepz})$ **13** and **14** are partly ionized in CH_2Cl_2 solution whereas the derivative **15** is a non-electrolyte in the same solvent. The 2:1 complexes **3–6** and **15** for which an ionic structure has been hypothesized in the solid state likely undergo a dissociation with concomitant re-association of the O-donor coordinating anion (Eq. (2)).



3.2. Spectroscopy

3.2.1. IR spectra

Selected IR data of the free donors and their corresponding Ag(I) complexes are listed in Section 2. In the regions $3200\text{--}3000\text{ cm}^{-1}$ and $1650\text{--}1500\text{ cm}^{-1}$, the ligands exhibit weak bands typical of C–H stretching and a number of more intense absorptions due to ring breathing modes, respectively [7]. These absorptions are not markedly shifted upon coordination of the ligand to Ag(I), suggesting a weak influence of the complexation on the absorptions within the donor.

The perchlorato derivatives **4**, **7** and **13**, having a 2:1 ligand to metal ratio, show a strong and broad absorption at approximately $1100\text{--}1080\text{ cm}^{-1}$, and a sharp medium or strong absorption at approximately 625 cm^{-1} . These vibrations indicate the presence of ionic perchlorato groups [8] in accordance with the proposed structures (see below). On the other hand, the perchlorato derivatives **1** and **10**, with 1:1 ligand to metal ratio show two or three strong and broad absorptions at approximately $1130\text{--}1070\text{ cm}^{-1}$ and sharp medium or strong absorption at approximately 625 cm^{-1} . These vibrations indicate the presence of perchlorato groups coordinated to silver in accordance with the structures proposed. In the spectrum of **1** a broad absorption at approximately 3560 cm^{-1} is due to the O–H stretching of the likely coordinated methanol molecule.

The nitrate derivatives **2**, **5**, **8**, **11** and **14** show broad absorptions in the range $1310\text{--}1400\text{ cm}^{-1}$ and a strong absorption at approximately $700\text{--}768\text{ cm}^{-1}$. The IR spectra may be indicative of the coordination mode of the nitrate groups [9], but in our case the NO_3 absorptions are overlapped with some absorptions due to the N_3 -donor ligand, so that the spectroscopic data does not afford reliable information.

The derivatives **3**, **6**, and **15** present some sharp absorptions between 1100 and 1000 cm^{-1} , typical of ionic RSO_3^- groups, whereas in the spectra of **9** and **12** the absorptions are more complex, as are those in derivatives containing coordinated RSO_3^- groups [10].

3.2.2. NMR spectra

The ^1H NMR spectra of the ligand and of the Ag(I) complexes (**1–15**) were recorded in CDCl_3 and, for

some derivatives, in CD_3OD and DMSO, as dictated by solubility considerations.

In the spectra of the derivatives of $\text{CH}(3,5\text{-Me}_2\text{pz})_3$ **4–6** and $\text{HC}(3,4,5\text{-Me}_3\text{pz})_3$ **7–9**, the Δ values (Δ = difference in chemical shift for the same type of proton in the free base and in its Ag(I) complex) are small, consistent with a large dissociation of the complexes in solution ($\Delta = 0.21\text{--}0.25\text{ ppm}$ for the methyls in the 3- and 5-positions of the pyrazole ring; $\Delta = 0.1\text{--}0.2\text{ ppm}$ for the bridging C–H proton in the $\text{CH}(3,5\text{-Me}_2\text{pz})_3$ derivatives).

In the derivatives of $\text{CH}(\text{pz})_3$ **1–3** and $\text{CH}(4\text{-Mepz})_3$ **10–12**, the Δ value is in the range $0.3\text{--}0.5\text{ ppm}$ for the protons in the 3 and 5 positions of the pyrazole ring, whereas Δ for the bridging C–H proton is in the range $0.2\text{--}1.1\text{ ppm}$, consistent with the existence of the complexed species in solution and suggesting that these ligands are better donors towards Ag(I) acceptors relative to ligands having methyl groups nearest to the coordination center.

Finally, it is of interest to observe that the greater Δ ($0.6\text{--}0.8\text{ ppm}$) values for the 5-CH protons have been found in the derivatives of $\text{CH}(3\text{-Mepz})_2(5\text{-Mepz})$ **13–15**.

In the spectra of derivatives **3**, **6**, **9**, **12** and **15** the resonance due to the methanesulphonate protons falls in the range $2.76\text{--}2.92\text{ ppm}$.

In all complexes only one signal is detected for each equivalent group of protons (or for the corresponding carbon atoms) showing that the boat-shaped six-membered rings are not rigid, the rings formed upon chelation becoming magnetically equivalent through rapid inversion or breaking of the Ag–N bonds. Our hypothesis has been supported by ^1H NMR experiments. For example the proton NMR spectrum of derivative **5**, recorded also at $-50\text{ }^\circ\text{C}$ both in the presence or absence of excess N_3 -donor ligand, exhibits only one set of signals and the chemical shifts were in the middle between those of the pure ligand and those of the starting complex.

The spectra of the 1:1 derivatives **1**, **2** and **10**, recorded in DMSO because of solubility considerations, show a line-width typical of a polynuclear structure, as in the case of **2**, also confirmed by single crystal X-ray studies.

The ^{13}C NMR spectra of the ligands and of the Ag(I) complexes (**1–15**) were recorded in CDCl_3 or DMSO. The carbon ring signals are shifted downfield upon complexation; negligible displacement was observed for the methyl carbons and a displacement to higher field was always observed for the CH bridging carbons, this displacement ranging from approximately $2\text{--}3\text{ ppm}$ in derivatives of $\text{CH}(4\text{-Mepz})_3$ to approximately 10 ppm in the derivatives containing the more sterically hindered ligands $\text{CH}(3,4,5\text{-Me}_3\text{pz})_3$ and $\text{CH}(3,5\text{-Me}_2\text{pz})_3$.

3.3. Crystallography

The results of the two single-crystal X-ray studies provide examples of complexes of $\text{AgNO}_3 \cdot \text{L}$ ($\text{L} = (\text{R}_n\text{pz})_3\text{CH}$) 1:1 and 1:2 stoichiometries, for $\text{R}_n = \text{H}_n$ and $\text{R}_n = 3,5\text{-Me}_2$, respectively.

$[\text{Ag}(\text{NO}_3)(\text{pz})_3\text{CH}]$ (1:1) (**2**) crystallizes with two formula units devoid of crystallographic symmetry as the asymmetric unit of the complex which is an infinite, unsolvated, two-dimensional polymer lying parallel to the *ac* plane (Fig. 4). The two independent silver atoms have different environments (Table 1(a)) with both neutral ligands and anionic nitrates playing a role in knitting symmetry related metal atoms into the polymer sheet. $\text{Ag}(2)$ has a tris(bidentate) environment, comprising pairs of pyrazolate N(2) donors from each of the independent pz_3CH ligands coordinating as chelates (nitrate 2 being the third through O(21,22)) with the third pyrazolate ring pendant and coordinating to an $\text{Ag}(1)$ atom in each case. The chelate from ligand 2 is more symmetrically coordinated than that from ligand 1, with the silver atom more nearly coplanar with the pyrazolate rings. The nitrate chelation is slightly unsymmetrical, the more tightly bound O(21) bifurcating so that with O(23), feebly bound, it chelates also to $\text{Ag}(1)$. Of the nitrate oxygens O(11) is the most tightly bound, pendant as a terminal ligand from $\text{Ag}(1)$ also; the environment of $\text{Ag}(1)$ is thus $\text{Ag}(\text{bidentate})_3(\text{unidentate})_3$.

By contrast only one half of the formula unit of the ionic 1:2 adduct $[\text{Ag}\{(\text{3,5-Me}_2\text{pz})_3\text{CH}\}_2]\text{NO}_3 \cdot \text{H}_2\text{O}$ (**5**), comprises the asymmetric unit of that structure, the cation disposed with the silver atom on a crystallographic inversion center (Fig. 5) and the anion modeled as disordered about another in space group $P2_1/c$. Here, each ligand behaves as a tripod (Table 1(b)), albeit seemingly rather uncomfortably accommodating interligand substituent clashes, particularly evident in the deviation of the silver atom out of ligand plane 3 (the plane with the longest Ag-N bond). The overall lattice disposition is similar to but not isomorphous to those recorded for numerous other $[\text{M}(\text{N}_3\text{-tripod})_2](\text{oxyanion})_2$ arrays [11].

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 172668–172669. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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