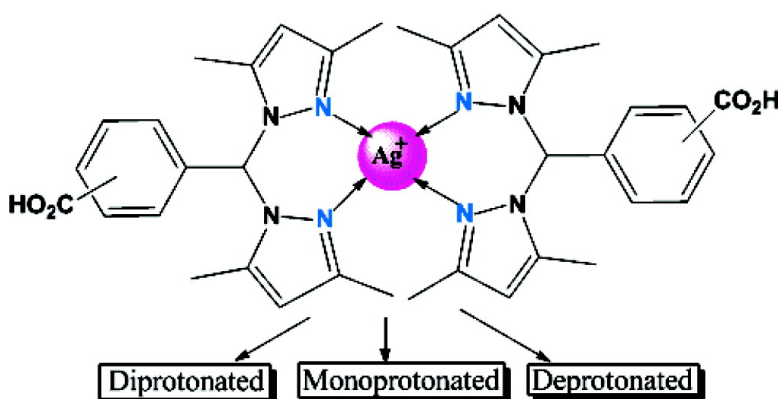


Article

Self-Assembly of Silver(I) Coordination Polymers Formed through Hydrogen Bonding with Ditopic Heteroscorpionate Ligands

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Self-Assembly of Silver(I) Coordination Polymers Formed through Hydrogen Bonding with Ditopic Heteroscorpionate Ligands

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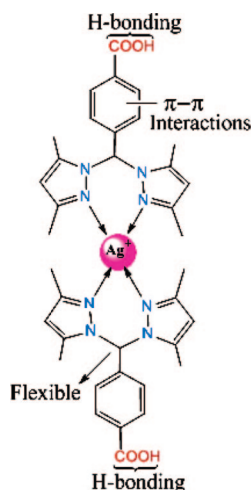
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ABSTRACT: Eight coordination polymers of silver Ag(I) derived from bidentate coordinating heteroscorpionate ligands, (4-carboxyphenyl)bis(3,5-dimethylpyrazolyl)methane (L4c) and (3-carboxyphenyl)bis(3,5-dimethylpyrazolyl)methane (L3c), have been synthesized and characterized by X-ray diffraction, ESI-MS, IR spectroscopy, and elemental analysis. By varying the solvent polarity, the protonation state of the uncoordinated carboxylate groups and hence their solid-state interactions can be controlled. While the silver monomers (tectons) possess chirality due to the asymmetric coordination of the achiral ligands to the silver ion, all of the solid-state materials were isolated as racemic mixtures.

Introduction

The growing interest in the crystal engineering of silver coordination polymers is not only because of their fascinating molecular structures, but also a result of their potential application as gas storage,¹ antimicrobial,² conductive material,³ luminescent,⁴ and magnetic materials.⁵ In addition, self-assembly of flexible achiral ligands with silver ions has produced interesting single, double, triple, and circular helicate systems that have attracted increased attention because of possible applications in materials science.⁶



Most higher order solid-state structures based on coordination polymers utilize stable coordinate covalent bonds.⁷ However, a variety of different noncovalent interactions such as hydrogen bonding and π - π stacking can also be employed to this end.⁸ Of these the hydrogen bond is the strongest, most selective, and directional of these noncovalent interactions and thus potentially an effective organizing interaction for designing and controlling solid-state structures.⁹ In particular, the carboxylic acid group has been widely employed as a linking unit between coordination monomers because of its strong tendency for self-complementarity.¹⁰ Our approach has been to make use of ditopic heteroscorpionate ligands, created by modifications to originally facially coordinating tripodal scorpionate and het-

eroscorpionate parents to produce different coordination polymers.¹¹ It is hoped that a thorough understanding of ligand design and complexation reaction conditions will allow us to increase the possibility of generating functional polymers. However, at present our capability of predicting and controlling these interactions to produce coordination polymers is still a very great challenge. Thus in previous work, we have shown that these new heteroscorpionates can coordinate a number of divalent metals only through the pyrazole nitrogen of the ligand leaving the uncoordinated carboxylic acid groups free to engage in hydrogen bonding, but only under very specific conditions.¹² To increase the predictability of the outcome of the reactions, as well to increase the range of conditions we could operate under, we choose to move from divalent Zn(II), Co(II), and Ni(II) to monovalent silver(I). There were two reasons for this choice. The first is that complexes of silver(I) have extensively been reported as building blocks for the self-assembly of supramolecular coordination polymers of various dimensionality in the solid state.¹³ Second silver(I) has been shown to have an extremely strong preference to coordinate to aromatic nitrogen donors over those of harder oxygen ligands. Thus, the synthesis and reactivity of silver(I) with nitrogen heterocyclic ligands have been investigated extensively.¹⁴ Particularly relevant is the extensive chemistry of silver(I) with different bis(pyrazolyl)borate and methanes in which the silver atoms are invariably coordinated solely through the pyrazole nitrogen of the ligand.¹⁵ Herein we describe the preparation and structural characterization of eight coordination polymers of silver(I) where the pyrazole nitrogen of the ligands are bound asymmetrically to the silver(I) cation, producing chiral silver monomers (tectons) that leave the carboxylic groups uncoordinated and free to engage in intermolecular hydrogen bonding.¹⁶ The expanded reaction conditions available with this approach allows us to control the protonation state of the carboxylate groups without engendering their coordination to the silver thereby making it possible to prepare 2 L:1 M complexes where the carboxylate groups are either both protonated, one protonated and one deprotonated, or both deprotonated. The result of these changes in the protonation state of the carboxylate group on the solid-state structures is discussed.

Experimental Procedures

Materials. All chemicals and solvents used during the syntheses were reagents grade. Bis(3,5-dimethylpyrazolyl)ketone was prepared

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Table 1. Crystallographic Data and Parameters for [Ag(HL4c)(L4c)] (1), [Ag(HL4c)(L4c)]·1.33H₂O (2), [Ag(HL4c)₂]ClO₄ (3), [Ag(HL3c)₂]NO₃·2H₂O (4), [Ag(HL3c)₂]SbF₆·3THF (5), [Ag(HL3c)₂]ClO₄·3THF (6), [Ag(HL3c)CH₃CN]BF₄ (7), and Ag[Ag(L3c)₂]·2H₂O (8)

	1	2	3	4	5	6	7	8
molecular formula	C ₃₆ H ₃₈ N ₈ O ₄ Ag	C ₃₆ H ₃₈ N ₈ O _{5.33} Ag	C ₃₆ H ₃₈ ClN ₈ O ₈ Ag	C ₃₆ H ₃₈ N ₉ O ₉ Ag	C ₄₈ H ₆₂ N ₈ O ₇ F ₆ SbAg	C ₄₈ H ₆₂ N ₈ ClO ₁₁ Ag	C ₂₀ H ₂₂ N ₅ O ₂ BF ₄ Ag	C ₃₆ H ₃₈ N ₈ O ₆ Ag ₂
fw	755.62	775.95	854.06	848.62	1206.68	1070.38	559.11	894.48
temp (K)	240(2)	298(2)	240(2)	240(2)	240(2)	240(2)	240(2)	240(2)
cryst system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
space group	C2/c	R3c	C2/c	P2 ₁ /n	C2/c	C2/c	P1	P2 ₁ /n
a (Å)	14.371(3)	20.9587(6)	15.040(7)	11.865(2)	41.151(2)	40.388(9)	10.1023(8)	11.079(12)
b (Å)	14.218(3)	20.9587(6)	22.925(7)	14.349(3)	11.2074(6)	11.245(2)	10.9760(9)	25.098(3)
c (Å)	17.119(4)	47.752(3)	16.887(6)	24.268(5)	26.9455(16)	25.791(6)	11.3498(9)	13.4274(15)
α (deg)	90	90	90	90	90	90	107.631(4)	90
β (deg)	93.107(13)	90	112.68(2)	95.609(9)	120.300(3)	118.900(19)	90.375(5)	92.846(4)
γ (deg)	90	120	90	90	90	90	92.876(5)	90
V (Å ³), Z	3492.7(13), 4	18165.8(13), 18	5372(3), 4	4112.2(15), 4	10729.5(10), 8	10255(4), 8	1197.56(17), 2	3729.1(7), 4
μ (mm ⁻¹)	0.628	0.548	0.469	0.551	0.944	0.510	0.898	1.106
δ _{calc} (g/cm ³)	1.437	1.277	1.056	1.371	1.494	1.387	1.551	1.593
F(000)	1560	7194	1752	1744	4912	4464	562	1808
size (mm ³)	0.2 × 0.2 × 0.2	0.3 × 0.3 × 0.2	0.8 × 0.7 × 0.1	0.2 × 0.2 × 0.2	0.4 × 0.4 × 0.3	0.7 × 0.1 × 0.1	0.3 × 0.2 × 0.1	0.3 × 0.3 × 0.3
h,k,l ranges collected	−19→18, −19→19, −23→22	−24→22, −24→24, −54→54	−22→14, −31→33, −20→25	−11→11, −13→13, −23→23	−54→39, −14→12, −35→36	−46→46, −13→12, −29→29	−11→11, 12→12, −12→12	−12→12, −22→28, −15→15
θ range (deg)	2.84–29.34	2.33–24.14	2.61–32.13	2.33–20.63	2.07–28.37	2.22–24.46	2.73–23.09	2.44–24.28
reflections collected	32562	76583	53962	41495	50674	82208	14025	52087
independent reflections	4683	3218	9087	3938	13299	8413	3322	6024
parameters	223	228	245	496	642	643	298	469
data/parameter	21	14.11	37.09	7.94	20.71	13.08	11.14	12.84
R (F) ^a	0.0345	0.0443	0.0741	0.0779	0.0631	0.0552	0.0396	0.0683
R _w (F ²) ^b	0.0908	0.1581	0.2379	0.2061	0.1600	0.1366	0.1072	0.1744
GOFFw ^c	1.035	1.153	1.073	1.109	1.023	1.025	1.029	1.116
largest diff peak and hole (e/Å ³)	0.828 and −0.380	0.878 and −0.359	1.761 and −0.472	1.494 and −1.005	1.460 and −1.686	0.718 and −0.540	0.63 and −0.374	1.809 and −2.048

^a $R = [\sum |\Delta F| / \sum |F_o|]$ for $[I > 2\sigma(I)]$. ^b $R_w = [\sum w(\Delta F)^2 / \sum w F_o^2]$ for $[I > 2\sigma(I)]$. ^c Goodness of fit on F^2 .

Table 2. Selected Bond Lengths (Å) for [Ag(HL4c)(L4c)] (1), [Ag(HL4c)(L4c)]·2H₂O (2), [Ag(HL4c)₂]ClO₄ (3), [Ag(HL3c)₂]NO₃·2H₂O (4), [Ag(HL3c)₂]SbF₆·3THF (5), [Ag(HL3c)₂]ClO₄·3THF (6), [Ag(HL3c)CH₃CN]BF₄ (7) and Ag[Ag(L3c)₂]·2H₂O (8)

	1	2	3	4	5	6	7	8
Ag(1)–N(1)	2.2847(16)	2.339(3)	2.217(3)	2.278(9)	2.383(4)	2.402(4)	2.310(3)	2.397(6)
Ag(1)–N(1)#1	2.2847(16)	2.339(3)	2.217(3)					
Ag(1)–N(3)	2.3961(18)	2.343(3)	2.429(3)	2.380(9)	2.291(4)	2.283(4)	2.244(3)	2.282(6)
Ag(1)–N(3)#1	2.3961(18)	2.343(3)	2.429(4)					
Ag(1)–N(5)				2.365(9)	2.403(4)	2.282(4)	2.134(4)	2.380(6)
Ag(1)–N(7)				2.290(9)	2.272(4)	2.390(4)		2.299(6)
Ag(2)–O(3)								2.509(6)
Ag(2)–O(4)								2.280(6)
Ag(2)#1–O(1)								2.586(5)
Ag(2)#1–O(2)								2.258(6)

according to the procedure described by Peterson et al.¹⁷ (4-Carboxyphenyl)bis(3,5-dimethylpyrazolyl)methane (L4c) and (3-carboxyphenyl)bis(3,5-dimethylpyrazolyl)methane (L3c) were prepared as previously described.¹⁸ Caution: perchlorate salts are dangerous (especially if they are dry) and should be handled with care!

Silver Complexes. (a) [Ag(HL4c)(L4c)] (1). An acetonitrile solution (4 mL) of ligand L4c (52.4 mg, 0.161 mmol) was added to an acetonitrile/methanol solution (3 mL/1 mL) of silver nitrate AgNO₃ (13.6 mg, 0.08 mmol); the mixture was then covered with aluminum foil and allowed to stir for 2 min. The resulting solution was layered with diethyl ether and colorless crystals were obtained after 1 day. An identical product was obtained when starting with silver benzoate instead of silver nitrate. Yield: 27.4 mg (45%). Anal. Calcd (Found) for [Ag(HL4c)(L4c)]·0.25H₂O, C₃₆H_{39.5}N₈O_{4.25}Ag, C, 56.88 (56.67); H, 5.24 (5.38); N 14.74 (14.54). IR (KBr pellets) ν /cm⁻¹: 3417, 2923, 1660, 1612, 1559, 1463, 1418, 1389, 1310, 1260, 1115, 1034, 879, 851, 797, 768, 712.

(b) [Ag(HL4c)(L4c)] (2). This complex was prepared in a manner analogous to that of complex 1 but using silver tetrafluoroborate (AgBF₄) in place of silver nitrate or benzoate. Identical products were obtained by using silver perchlorate (AgClO₄), silver hexafluoroantimonate (AgSbF₆), or silver nitrate (AgNO₃) in the presence of dilute aqueous ammonia in place of silver tetrafluoroborate. Yield: 44 mg (72%). Anal. calcd (found) for [Ag(HL4c)(L4c)]·2H₂O, C₃₆H₄₃N₈O₆Ag, C, 54.62 (54.41); H, 5.47 (5.19); N 14.15 (14.07). IR (KBr pellets)

ν /cm⁻¹: 3419, 2933, 1650, 1614, 1559, 1463, 1418, 1389, 1310, 1260, 1115, 1034, 879, 851, 797, 768, 712.

(c) [Ag(HL4c)₂]ClO₄ (3). A tetrahydrofuran solution (4 mL) of ligand L4c (51.2 mg, 0.158 mmol) was added to a tetrahydrofuran (4 mL) solution of silver perchlorate (16.4 mg, 0.079 mmol), and the mixture covered with aluminum foil, and stirred for 5 min. The colorless solution was layered with hexanes at room temperature and X-ray quality crystals were obtained after a period of 2 days. Yield: 41.8 mg (62%). Anal. Calcd (found) for [Ag(HL4c)₂]ClO₄·0.5H₂O, C₃₆H₄₁N₈O_{8.5}ClAg, C: 49.98 (50.02), H: 4.78 (5.10), N: 12.95 (12.70). IR (KBr pellets) ν /cm⁻¹: 3449, 2981, 1692, 1613, 1560, 1459, 1421, 1385, 1321, 1294, 1258, 1184, 1095, 1042, 960, 876, 801, 758, 710, 623.

(d) [Ag(HL3c)₂]NO₃ (4). An acetonitrile/methanol (3 mL/1 mL) solution of ligand L3c (30.4 mg, 0.09 mmol) was added to a solution of silver nitrate (7.7 mg, 0.0045 mmol) in the same solvent, and the mixture was stirred for 1 min. The colorless solution was left to stand at room temperature, and X-ray quality crystals were obtained after a period of 6 days. Yield: 17 mg (43%). Anal. Calcd (found) for [Ag(HL3c)₂]NO₃·0.25H₂O, C₃₆H_{40.5}N₉O_{7.25}Ag, C: 52.53 (52.71), H: 4.96 (5.02), N: 15.31 (15.18). IR (KBr pellets) ν /cm⁻¹: 3418, 2923, 1701, 1558, 1384, 1318, 1248, 1188, 1032, 870, 825, 752, 709, 684.

(e) [Ag(HL3c)₂]SbF₆ (5). This complex was prepared in a manner analogous to that of complex 3 using silver hexafluoroantimonate and ligand L3c in place of silver perchlorate and ligand L4c, respectively.

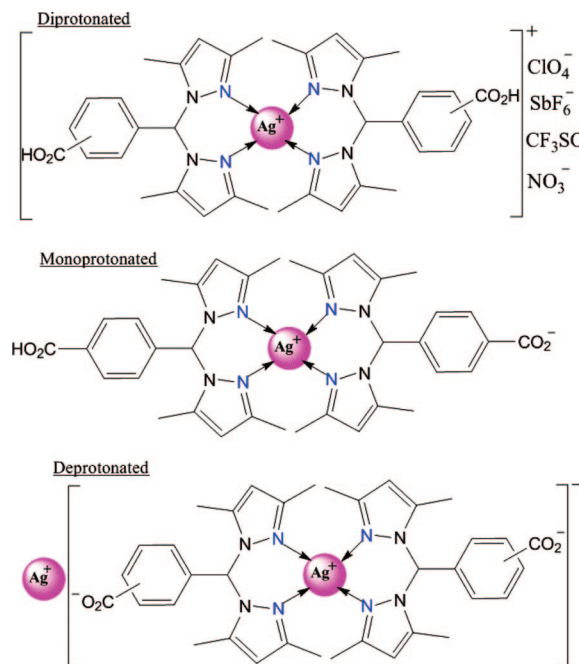


Figure 1. Schematic representation of three different protonation states of the silver(I) tectons formed from ligands L4c and L3c.

Yield: 46 mg (78%). Anal. calcd (found) for $[\text{Ag}(\text{HL3c})_2]\cdot\text{SbF}_6\cdot 2\text{THF}\cdot 0.5\text{H}_2\text{O}$, $\text{C}_{44}\text{H}_{37}\text{N}_8\text{O}_{6.5}\text{SbF}_6\text{Ag}$ C; 46.13 (46.03), H; 5.02 (5.09), N; 9.78 (9.51) IR (KBr pellets) ν/cm^{-1} : 3419, 2984, 1699, 1561, 1418, 1385, 1315, 1251, 1189, 1042, 871, 815, 752, 710, 660.

(f) $[\text{Ag}(\text{HL3c})_2]\text{ClO}_4$ (**6**). This complex was prepared in a manner analogous to that of complex **3** using ligand L3c in place of ligand L4c. Yield: 65 mg (72%). Anal. Calcd (found) $[\text{Ag}(\text{HL3c})_2]\cdot\text{ClO}_4\cdot 2.5\text{THF}\cdot 0.5\text{H}_2\text{O}$, $\text{C}_{46}\text{H}_{61}\text{N}_8\text{O}_{11}\text{ClAg}$ C; 52.85 (52.59), H; 5.88 (5.59), N; 10.72 (10.61). IR (KBr pellets) ν/cm^{-1} : 3449, 2924, 1718, 1560, 1449, 1420, 1385, 1249, 1186, 1108, 870, 792, 751, 709, 623.

(g) $[\text{Ag}(\text{HL3c})(\text{CH}_3\text{CN})]\text{BF}_4$ (**7**). A solution of ligand L3c (35.68 mg, 0.11 mmol) in acetonitrile/methanol (4 mL/2 mL) was added to an acetonitrile solution (4 mL) of silver tetrafluoroborate AgBF_4 (21.41 mg, 0.11 mmol). The mixture was covered with aluminum foil and stirred for 2 min. The colorless solution was left to stand at room temperature, and crystals were obtained after a period of 1 week. Yield: 38 mg (62%). Anal. Calcd (found) for $[\text{Ag}(\text{HL3c})(\text{CH}_3\text{CN})]\text{BF}_4$, $\text{C}_{20}\text{H}_{23}\text{N}_5\text{O}_2\text{BF}_4\text{Ag}$, C; 42.89 (43.03), H; 4.14 (4.25), N; 12.50 (12.38) IR (KBr pellets) ν/cm^{-1} : 3450, 2924, 2248, 1710, 1550, 1445, 1415, 1380, 1259, 1186, 1108, 870, 750, 721.

(h) $\text{Ag}[\text{Ag}(\text{L3c})_2]$ (**8**). An aqueous solution (3 mL) of silver perchlorate (14 mg, 0.067 mmol) was layered with methanol solution (3 mL) of ligand L3c (21.8 mg). Colorless crystals were obtained after 4 days. The same result was obtained by using Ag_2SO_4 or AgCF_3SO_3 in place of AgClO_4 . Yield: 33 mg (51%). Anal. calcd (found) for $\text{Ag}[\text{Ag}(\text{L3c})_2]\cdot 0.5\text{H}_2\text{O}$, $\text{C}_{36}\text{H}_{39}\text{N}_8\text{O}_{4.5}\text{Ag}_2$, C; 49.61 (49.83), H; 4.51 (4.69), N; 12.86 (13.01). IR (KBr pellets) ν/cm^{-1} : 3449, 2921, 1725, 1662, 1551, 1430, 1400, 1380, 1210, 1190, 875, 753, 710, 625.

Physical Methods. Elemental analyses were performed on all compounds by Numea Laboratories, San Diego, CA. All samples were dried in a vacuum prior to analysis. IR spectra were recorded as KBr disks on a ThermoNicolet Nexus 670 FT-IR spectrometer and are reported in wavenumbers. Electrospray mass spectra (ESI-MS) were recorded on an Agilent 6300 Ion Trap LC-MS mass spectrometer equipped with an ESI source. A HP computer with Agilent 6300 Series ion trap software version 5.3 was used for data acquisition and plotting. Isotope distribution patterns were simulated using the program IsoPro 3.0.

X-ray Crystallography. Crystals of complexes **1–8** data were mounted using nylon loops and paratone oil (Hampton Research), and placed in the cold stream of a Bruker X8 APEX CCD diffractometer operating at 50 kV and 30 mA using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods or via the Patterson function, completed by subsequent difference Fourier syntheses, and

refined by full-matrix least-squares procedures on F^2 . All non-hydrogen atoms were refined with anisotropic displacement coefficients and treated as idealized contributions using a riding model except as noted. Because of potentially complex hydrogen bonding interactions, idealized generation of hydrogen atoms on some of the solvent molecules and/or the protonated carboxylate groups was deemed inappropriate, and thus their contributions were ignored unless such atoms could be unambiguously located on final difference maps in which case they were subsequently refined to ride on their respective heavy atom. Note: Crystals of **4** diffracted relatively poorly, giving rise to weak data that was only collected out to ca. 40° in 2θ . All software and sources of the scattering factors are contained in the SHELXTL 6.12 program library (G. Sheldrick, Siemens XRD, Madison, WI).¹⁹ Crystallographic data for **1–8** are listed in Table 1, and selected bond lengths and angles for all compounds are given in Tables 2–4. ORTEP diagrams of **1–8** can be found in the Supporting Information.

Results and Discussion

Synthesis and Characterization. In early work, we showed that the reaction of the N_2O heteroscorpionate ligands designated L4c and L3c with different metal salts produced various dinuclear species.^{18,20} In all of these cases a deprotonated carboxylate group of the heteroscorpionate ligand is involved in coordination to the metal ion. In later work, we showed that the carboxylic acid group can keep protonated by varying the reaction conditions (i.e., decreasing the pH or by decreasing the solvent polarity) so that they no longer coordinate to the metal ions and are thus free to engage in either self-complementary H-bonding interactions or H-bonding with solvent molecules or counterions.¹² However the conditions under which the carboxylate groups remain protonated and thus uncoordinated are limited. Here we take advantage of the soft Lewis acidic nature of the silver(I) ion which binds exclusively to the softer pyrazole nitrogen donors of the ligand, irrespective of the protonation state of the carboxylic acid group, which remains uncoordinated.¹⁶ Thus we have been able to isolate complexes of the general stoichiometry “ AgL_2 ” in all three of its possible protonation states, that is, $[\text{Ag}(\text{HL})_2]^+$, $[\text{Ag}(\text{HL})(\text{L})]^\circ$, and $[\text{AgL}_2]^-$ (Figure 1). The overall protonation state of the complex affects the solid-state interactions, which are described in detail below.

Completely protonated complexes of the type $[\text{Ag}(\text{HL})_2]^+$ were obtained for both ligands L4c and L3c by using pure tetrahydrofuran as a solvent. Analyses of **3–6** by ESI-MS in acetonitrile were all similar and showed that the predominant species were always the simple AgL_2^+ cation. The monoprotonated state of the complex, that is, $[\text{Ag}(\text{HL})(\text{L})]^\circ$ could be obtained by using a mixture acetonitrile/methanol, though we were unable to isolate complexes of this type for the ligand L3c. We analyzed the ESI-MS spectra of the complex(es) present in the mixed methanol/acetonitrile solvent system with the L4c ligand in positive ion mode (Figure 2). The mass spectrum of this solution shows two clean high mass clusters allowing us to identify species in solution that were not amenable to solid-state structural analysis by X-ray crystallography. The first mass cluster is centered at 971 amu and has an isotope pattern indicative of a trinuclear $[\text{Ag}_3(\text{L4c})_2]^+$ cation associated with the completely deprotonated state. The other high mass cluster is centered at 863 amu and has an isotope pattern that is consistent with the $[\text{Ag}_2(\text{L4c})_2]^+$ cation. These results indicate that there may be an equilibrium between the monoprotonated and completely deprotonated states in solution.

The anionic complexes $[\text{AgL}_2]^-$, with completely deprotonated carboxylates, were obtained using aqueous methanol as a solvent. In this case, we were only able to get a crystal structure of the deprotonated species with the L3c ligand and

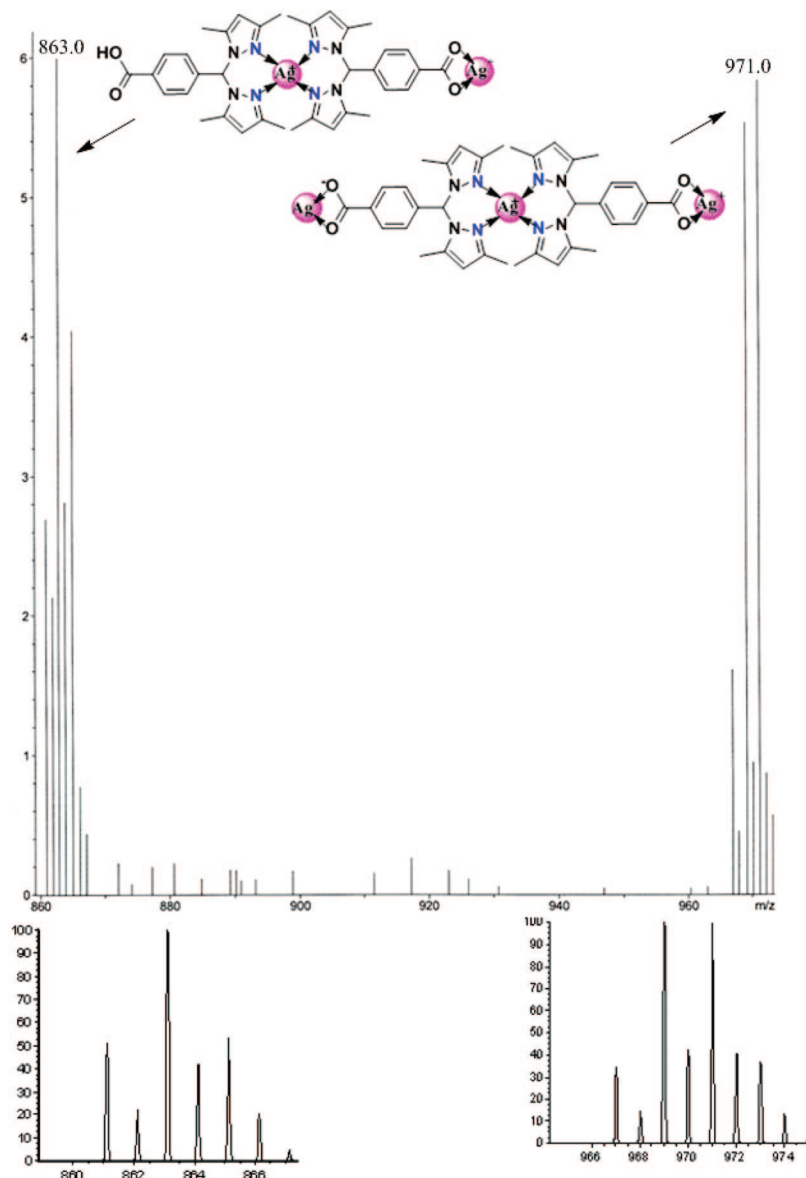


Figure 2. Positive-ion ESI-MS of a solution of $AgNO_3$ and L4c in acetonitrile/methanol. The upper frame shows the peak clusters associated with the structures $[Ag_2(L4c)_2]^+$ and $[Ag_3(L4c)_2]^+$. The lower frame shows the calculated isotope distribution pattern expected for these fragments.

silver(I) as the cation; however, the formation of an analogous complex with L4c was confirmed in solution by ESI-MS (vide supra).

Solid-State Structures and Crystal Packing. The overall structure of all of these “ AgL_2 ” complexes, regardless of protonation state, is best described as being pseudotetrahedral, that is, intermediate between perfect square planar (dihedral angle between planes of 0°) and idealized tetrahedral (dihedral angle between planes of 90°). Although the ligands L4c and L3c are achiral, the silver monomers AgL_2 (tectons) possess chirality due to the asymmetric coordination of the ligand to the silver ion. However all the solid-state materials we isolated are racemic mixtures, although the means by which this is achieved differ. Thus, hydrogen bonding and other interactions between the tectons leads to coordination polymers with alternating M (left handed) and P (right handed) monomer units that form meso helical chains (complexes **1** and **3**), racemic mixtures of pure P & M metallocycle trimers (**2**), or racemic mixtures of linear pure P & M helical polymers (**8**). The orientation of carboxylic acid groups that lead to these various structures are associated with the dihedral angle between the

pyrazole nitrogen around the silver cation. Thus in the situation where both the carboxylate groups are protonated and hence uncharged (i.e., complex **3**), the dihedral angle is 81.53° and the mesohelical polymer is isolated. In the half-protonated state the solid-state structure depends critically on the reaction conditions. With the ligand L4c and starting with silver nitrate or benzoate, the product has a dihedral angle of 76.64° , which leads once again to the mesohelical polymer (i.e., complex **1**). However with the same ligand but using silver perchlorate or hexafluoroantimonate leads to complex **2**, which has a smaller dihedral angle of 65.95° . This orientation leads to a racemic mixture of metallocycle trimers. Various factors such as the presence of water appear to be involved in this change in structure as silver nitrate in the presence of dilute aqueous ammonia gives the racemic mixture of metallocycle trimers, while silver nitrate in strictly organic solvents yields the 1-D meso helical polymers. When both carboxylate groups are deprotonated as in **8**, the dihedral angle is the smallest of all the complexes at 62.79° , and in this case a racemic mixture of linear P & M coordination helices was obtained.

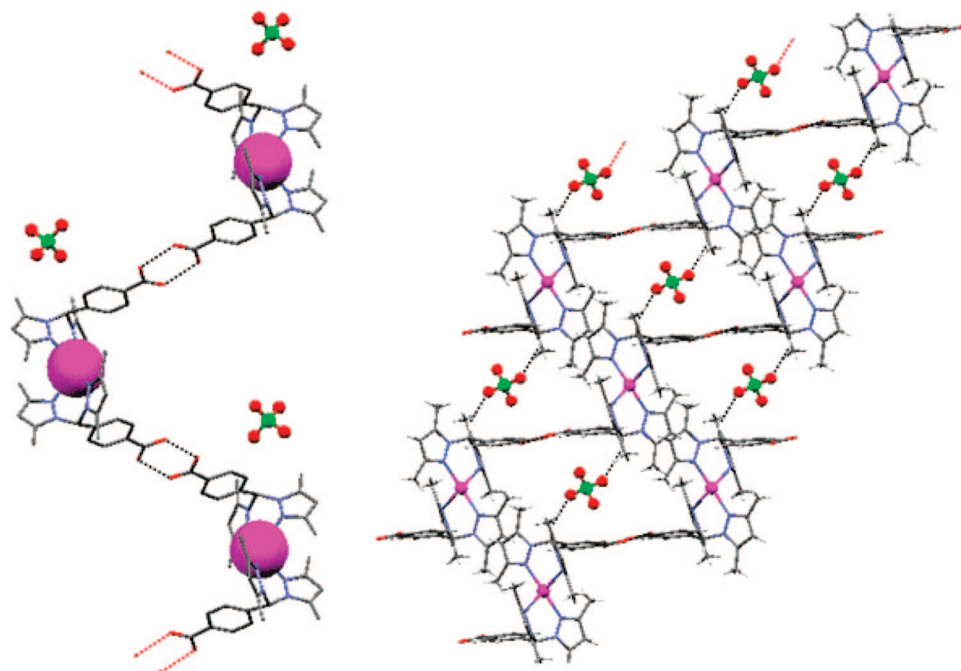


Figure 3. Perspective view of a 1-D meso helical chain of $[\text{Ag}(\text{HL4c})_2]\text{ClO}_4$ (**3**) (left). Packing diagram of (**3**) as seen along the crystallographic b (right). Hydrogen bonds are shown as dotted lines.

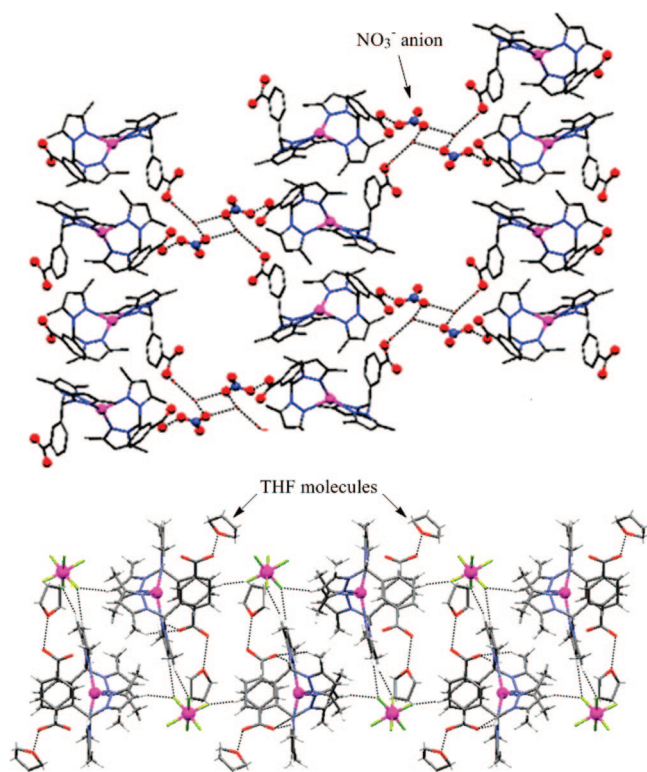


Figure 4. Crystal packing diagram for $[\text{Ag}(\text{HL3c})_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$ (**4**) as seen along the crystallographic c axis. Hydrogen bonds among carboxylic group, solvent molecules, and nitrate are shown as dotted lines (top). Crystal packing diagram for $[\text{Ag}(\text{HL3c})_2]\text{SbF}_6$ (**5**) as seen along the crystallographic b axis. Interactions $\text{O} \cdots \text{H} \cdots \text{O}$ and $-\text{CH} \cdots \text{F}$ are shown as dotted lines (bottom).

The Diprotonated State. The reaction of the ligand L4c with silver perchlorate (AgClO_4), silver hexafluoroantimonate (AgSbF_6), or silver trifluoromethanesulfonate (AgCF_3SO_3) all produced a coordination polymer with a $[2\text{HL}/\text{Ag}/\text{Anion}]_\infty$ ratio.

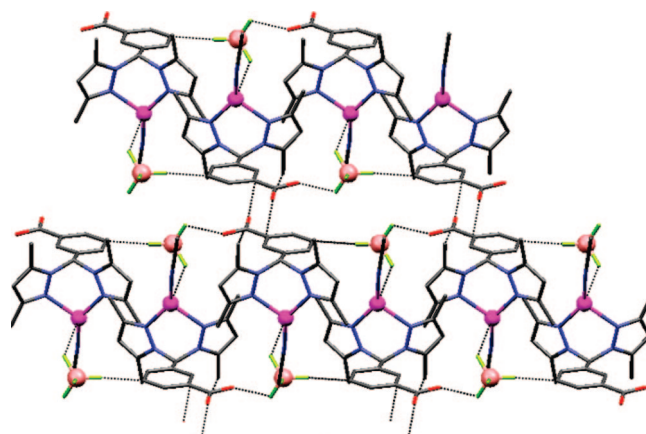


Figure 5. Crystal packing diagram of $[(\text{HL3c})\text{Ag}(\text{CH}_3\text{CN})]\text{BF}_4$ (**7**) as seen along the crystallographic a axis. Interactions $\text{OH} \cdots \text{F}$, $\text{CH} \cdots \text{F}$, $\text{F} \cdots \text{Ag}$, and π - π stacking are shown as dotted lines.

Table 3. Selected Angles (deg): $[\text{Ag}(\text{HL4c})(\text{L4c})]$ (**1**), $[\text{Ag}(\text{HL4c})(\text{L4c})]2\text{H}_2\text{O}$ (**2**), and $[\text{Ag}(\text{HL4c})_2]\text{ClO}_4$ (**3**)

	1	2	3
$\text{N}(3)-\text{Ag}(1)-\text{N}(1)$	80.95(6)	81.35(12)	86.72(12)
$\text{N}(3)\#1-\text{Ag}(1)-\text{N}(1)\#1$	80.95(6)	81.35(12)	86.72(12)
$\text{N}(1)-\text{Ag}(1)-\text{N}(3)\#1$	111.34(6)	112.75(12)	108.73(12)
$\text{N}(1)\#1-\text{Ag}(1)-\text{N}(3)$	111.34(6)	112.75(12)	108.73(12)
$\text{N}(1)-\text{Ag}(1)-\text{N}(1)\#1$	158.54(9)	147.08(18)	154.7(2)
$\text{N}(3)-\text{Ag}(1)-\text{N}(3)\#1$	112.61(8)	130.70(17)	106.06(17)

These complexes show the same environment about the silver Ag(I) center, which is coordinated by the four pyrazole nitrogen of the chelating ligand L4c with a structural index parameter (τ_4)²¹ of 0.68. Silver–nitrogen bond lengths are asymmetric with values falling between 2.217 and 2.429 Å. The silver monomer (tecton) possesses chirality due to asymmetric coordination of the ligand L4c to the silver ion. Extensive self-complementary hydrogen bonds formed between the protonated carboxylic groups of adjacent molecules results in a solid-state polymer that contains alternating M (left handed) and P (right handed)

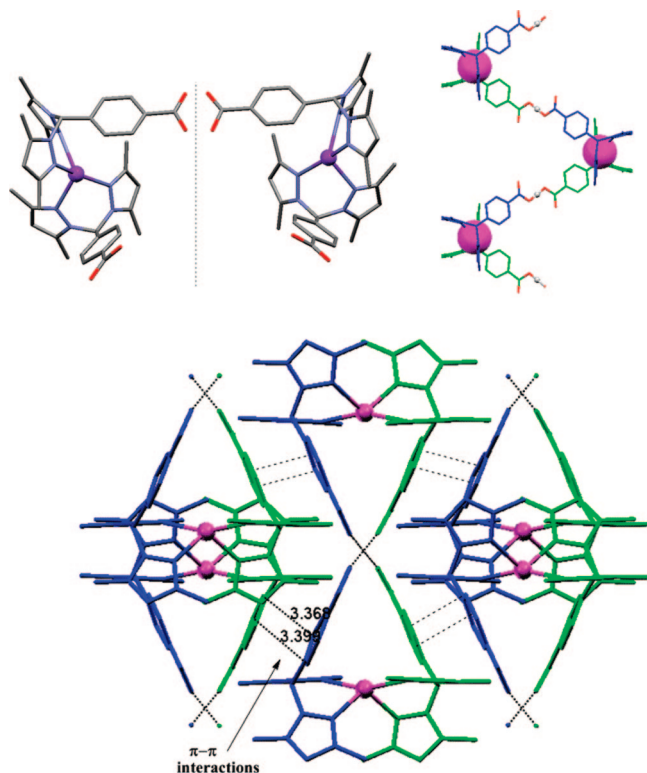


Figure 6. View of the silver monomer enantiomers with ligand L4c showing the asymmetric coordination (top left). Perspective view of a 1-D meso helical chain for $[\text{Ag}(\text{HL4c})(\text{L4c})]$ (**1**) (top right). Packing diagram of (**1**) as seen along the crystallographic c axis (bottom). The dotted lines indicate hydrogen bonds and π - π stacking interactions among these meso helical structures.

Table 4. Selected Angles (deg): $[\text{Ag}(\text{HL3c})_2][\text{NO}_3 \cdot 2\text{H}_2\text{O}]$ (**4**), $[\text{Ag}(\text{HL3c})_2][\text{SbF}_6 \cdot 3\text{THF}]$ (**5**), $[\text{Ag}(\text{HL3c})_2][\text{ClO}_4 \cdot 3\text{THF}]$ (**6**), $[\text{Ag}(\text{HL3c})\text{CH}_3\text{CN}][\text{BF}_4]$ (**7**), and $\text{Ag}[\text{Ag}(\text{L3c})_2] \cdot 2\text{H}_2\text{O}$ (**8**)

	4	5	6	7	8
N(3)-Ag(1)-N(1)	82.0(3)	81.68(14)	80.80(14)	86.84(12)	82.0(2)
N(5)-Ag(1)-N(1)	112.7(3)	114.60(15)	115.01(14)	127.29(15)	133.1(2)
N(7)-Ag(1)-N(1)	148.0(3)	117.02(14)	116.12(14)		108.7(2)
N(5)-Ag(1)-N(3)	120.9(3)	111.59(14)	150.10(15)	145.56(15)	113.0(2)
N(7)-Ag(1)-N(3)	114.0(3)	151.83(15)	115.54(14)		147.6(2)
N(7)-Ag(1)-N(5)	83.6(3)	80.95(14)	81.47(14)		82.5(2)
O(2)#2-Ag(2)-O(4)					150.4(2)
O(2)#2-Ag(2)-O(3)					152.8(2)
O(2)#2-Ag(2)-O(1)#2					53.64(18)
O(4)-Ag(2)-O(3)					54.30(18)
O(4)-Ag(2)-O(1)#2					139.6(2)
O(3)-Ag(2)-O(1)#2					119.47(17)

monomer (tecton) units forming a meso helical 1-D coordination chain. The anions (ClO_4^- , $^-\text{OSO}_2\text{CF}_3$, SbF_6^-) in these polymers are not directly coordinated to the silver cation, but rather form hydrogen bonds between acidic methine protons (distance $\text{O} \cdots \text{H}-\text{C}$ 2.475 Å) located on alternate polymer chains. Thus the overall 2-D structure consists of infinite meso polymeric chains held together by self-complementary hydrogen bonds between the carboxylate groups with the 1-D chains linked together by hydrogen bonding between the anions and methine protons of ligands on alternate chains (Figure 3).

With heteroscorpionate ligand L3c, complexes **4**, **5**, and **6** (nitrate, hexafluoroantimonate, and perchlorate salts respectively) all show the silver(I) is again coordinated to the four pyrazole nitrogens of the ligand in a pseudotetrahedral, four coordinate, geometry with index parameters (τ_4)²¹ of 0.64 (complex **4**), 0.56 (complex **5**), and 0.66 (complex **6**), respectively. The dihedral angle between N(1)-Ag(1)-N(3) and N(5)-Ag(1)-N(7) planes

is 73.58° in (**4**), 78.23° in (**6**), and 75.05° in (**5**), all of which are much closer to the 90° angle expected of a tetrahedron than the 0° expected for the alternate square planar description. The largest N-Ag-N angle varies from 148.0° in (**4**) to 158.6° in (**5**), while that of (**6**) is intermediary at 150.10°. The remaining angles are in the range between 82.0° to 122.2°. Silver-nitrogen bond lengths are once again asymmetric with values falling between 2.278 and 2.390 Å.

The crystal packing architecture of **4** consists of a 2-D network held together by hydrogen bonding between nitrate anion, solvent molecules, and carboxylic acid groups (Figure 4a). Meanwhile, the overall 2-D supramolecular structure of **5** is governed by a series of hydrogen bonding interactions between the fluorine or oxygen atoms of the counterion ($\text{CH} \cdots \text{X}$ ave. 2.51 Å). In addition to the interactions between the anions and silver complex, there is also hydrogen bonding between the carboxylic acid group of the ligand and a tetrahydrofuran of solvation, but these hydrogen bonds do not contribute to the development of a coordination polymer (Figure 4b). Indeed the H-bonding by the THF of solvation serves to "cap" the free carboxylate groups and prevents them from forming the strong self-complementary H-bonding seen in **3**. The same crystal packing was obtained with complex **6**. A comparison between the packing found for the identical complexes formed from the linear L4c ligand vs the angular L3c ligand under the same conditions (i.e., solvent tetrahydrofuran and anions SbF_6^- , ClO_4^- , and CF_3SO_3^-) clearly demonstrates the effect of ligand geometry. Thus the linear L4c ligand invariably leads to meso helical coordination polymers produced by strong self-complementary hydrogen bonding between the carboxylate groups, while the bent ligand (L3c) consistently leads to weakly linked 2-D structures where the carboxylate groups hydrogen bond to anions and/or solvent rather than to each other.

The structure of complex **7** is completely different from that of all the other complexes isolated in this study in that it has 1Ag:1 L rather than a 1Ag:2 L stoichiometry. In this case an acetonitrile is bound to the silver which is further coordinated only by the two pyrazole nitrogens of a single chelating L3c ligand leading to a geometry that can best be described as distorted trigonal planar. The largest N(3)-Ag(1)-N(5) angle opened up to 145.56° from the ideal trigonal planar, while the remaining angles are in the range from 86.85° to 127.27°. Ag-N_{pyrazole} bonds are longer (2.244 and 2.311 Å) as compared to the Ag-N_{acetonitrile} at 2.134 Å. The crystal packing of **7** shows that the BF_4^- anions take part in weak hydrogen bonding interactions ($\text{CH} \cdots \text{F}$ and $\text{OH} \cdots \text{F}$), which support the assembly by bridging between the coordination monomers $[\text{Ag}(\text{HL3c})\text{CH}_3\text{CN}]$. The $\text{CH} \cdots \text{F}$ are in the range of 2.30 Å, while the $\text{O} \cdots \text{H} \cdots \text{F}$ distance is 2.66 Å, $\text{F} \cdots \text{Ag}$ distance is 2.86 Å, and the π - π interactions are 3.35 Å (Figure 5).

The Monoprotonated State. For the reaction of ligand L4c with either silver benzoate ($\text{AgC}_6\text{H}_5\text{CO}_2$) or silver nitrate (AgNO_3) as a metal source, the polymer isolated, complex **1**, has a $[\text{HL}:\text{Ag}:\text{L}]_\infty$ ratio where charge considerations indicate one carboxylic group is protonated and the other deprotonated. On the other hand, using the same solvent ratio, but with silver tetrafluoroborate (AgBF_4), silver perchlorate (AgClO_4), silver hexafluoroantimonate (AgSbF_6), or a mixture of ($\text{AgNO}_3 + \text{NH}_4\text{OH}$) as a starting material results in a discrete trimeric product, complex **2** with stoichiometry $[\text{HL}:\text{Ag}:\text{L}]_3$. Selected distances and angles for the structures of **1** and **2** are shown in Tables 2 and 3. Single-crystal X-ray diffraction studies on the neutral complexes **1** and **2** reveal that these complexes possess a crystallographic center of inversion making only one-half of

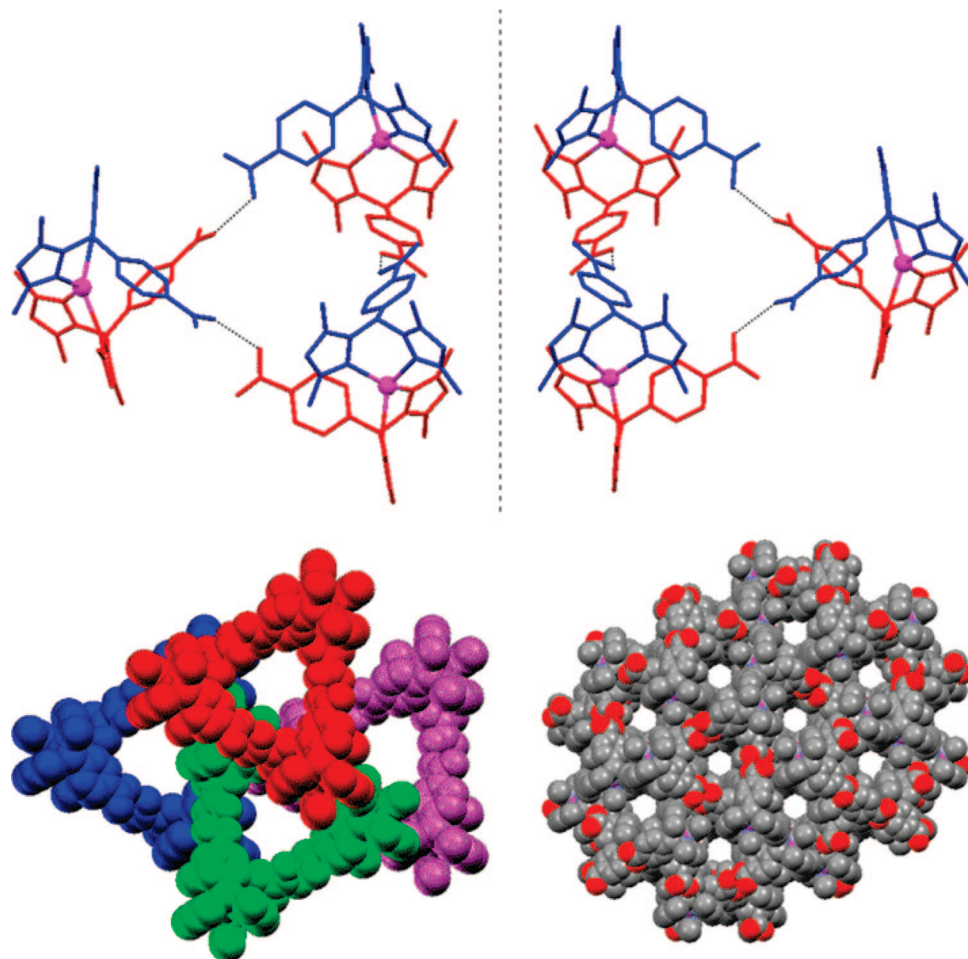


Figure 7. Perspective view of metalocycle trimer enantiomers (**2**) showing hydrogen bonds are shown as dotted lines (top). Schematic view of (**2**) showing chiral metalocycle trimer alternation packing diagram for (**2**) (bottom left) and space-filling representation (bottom right) as seen along the crystallographic *c* axis. Solvent molecules and hydrogen atoms have been omitted for clarity.

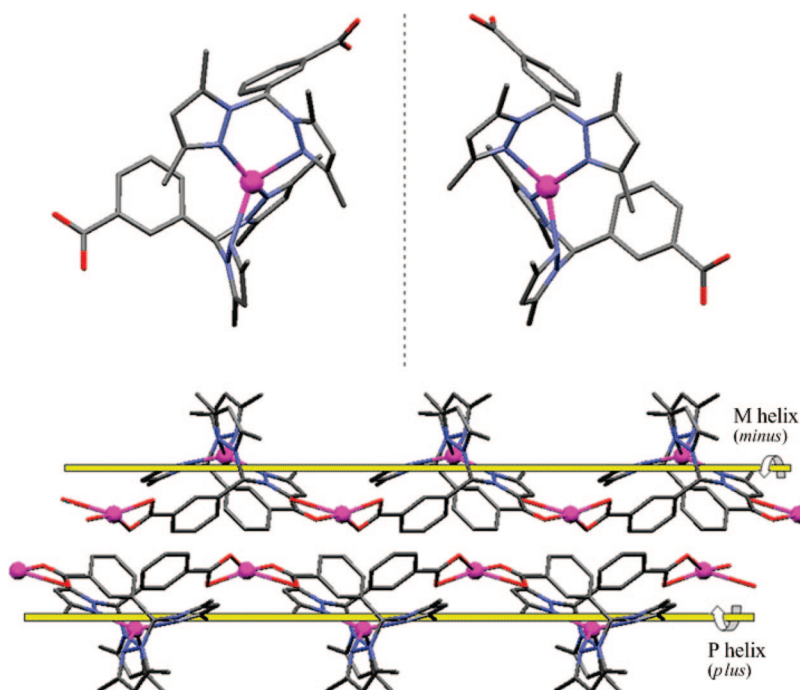


Figure 8. View of the enantiomers of the silver complex (**8**) with ligand L3c (top). Crystal packing diagram of the two chiral coordination polymer chains as seen along the crystallographic *c* axis (bottom). Solvent molecules and hydrogen atoms have been omitted for clarity.

these monomeric structures unique. Complex **1** crystallizes in space group $C2/c$, while complex **2** crystallizes in $R3c$. The index parameters (τ_4)²¹ are 0.63 and 0.58, respectively. Therefore, the geometry around silver ion in both cases can best be described as distorted tetrahedral. Silver–nitrogen bond lengths are decidedly asymmetric in complex **1** with values falling between 2.217 and 2.429 Å, while in complex **2**, the bond lengths are much more symmetric with values falling in the narrow range between 2.339 and 2.343. The largest N(1)–Ag(1)–N(1)#1 angle is 158.54° in **1** and 147.08° in **2**, while the remaining angles are in the range from 80.95 to 112.75(12)°. The dihedral angles between N(1)–Ag(1)–N(3) and N(1)#1–Ag(1)–N(3)#1 planes at 76.64° in (**1**) and 65.95° in (**2**) are much closer to the 90° angle expected of a tetrahedron, as compared to the 0° angle for the alternate square planar description.

While the molecular structure of the monomer units in **1** and **2** are very similar to each other and to those of the other protonated states, the crystal packing was completely different between them. The packing in **1** is governed by single hydrogen bonding interactions between the protonated and unprotonated carboxylic groups (av. O···H···O distance 2.44 Å). The overall assembly of this complex is achiral due to the alternation of P & M tectons in the chains, which results in the overall 1-D *meso* helical configuration. Each twist unit is participating in four intermolecular π – π stacking interactions between the aromatic rings (av. 3.32 Å) with neighboring helices along the *b*-axis direction (Figure 6). There is also interpenetration between these coordination polymers due to a perpendicular C–H··· π interaction with a distance of 2.774 Å' between the methyl group and aromatic ring of ligand L4c.

The packing in **2** is completely different, although it is again governed by single hydrogen bonding interactions among three chiral silver monomer complexes through protonated and unprotonated carboxylic acid groups (av. O···O 2.432 Å). These chiral ribbon triangle structures are held together by a series of weak, CH···O, C–H··· π , and π – π interactions. Space filling models indicate a hole of diameter 5–6 Å in the center of the triangle (Figure 7). Each chiral metallocycle triangle is surrounded by six other metallocycle triangles held together by pi interactions. The resulting packing contains alternating chiral metallocycle triangle units forming an overall racemic mixture.

The Unprotonated State. In complex **8** one silver ion is coordinated by four pyrazole nitrogens of the AgL₂ monomer unit, while the other, charge neutralizing, silver "cation" is coordinated by four oxygen from carboxylate groups of two different monomers. For both silver ions, the geometry can be best described as distorted tetrahedral. The carboxylate groups are linked to the silver cation in an anisobidentate fashion with the shorter distances Ag(2)#1–O(2) and Ag(2)–O(4) at 2.258(6) and 2.280(6) Å, respectively, while the longer distances are 2.509 and 2.586 Å. The dihedral angle between N(1)–Ag(1)–N(3) and N(5)–Ag(1)–N(7) at 62.79° is closer to the 90° angle expected of a tetrahedron than that of the dihedral angle between O(1)–Ag(2)–O(2) and O(3)–Ag(2)–O(4) of 67.56°. Although the reaction again generates chiral silver monomers (tectons), the packing is completely different from that seen in the other polymers (i.e., **1** and **3**). In this case there is an equimolar mixture of pure P (plus) and M (minus) linear 1-D helices forming a racemic mixture (Figure 8) rather than the alternating P and M tectons units that leads to the alternate *meso* helical arrangement.

Conclusions

In this work, eight silver complexes with the ditopic ligand L4c and L3c and different silver salts were prepared and

characterized. These silver monomer (tectons) have been demonstrated to yield a variety of new chiral silver complexes showing both discrete and polymeric architectures. The ultimate achirality of these architectures comes from the different disposition of the chiral silver building blocks. These polymeric structures remain quite unusual, and to date only a few examples of *meso*-helical coordination polymers²² and metallocycle triangles are known.²³ It is clear that that the packing of the [AgL₂] monomers (tectons) depends to a great extent on the orientation and protonation state of the carboxylate groups of the ligands, which in turn depend on solvent polarity, the metal salt utilized in their formation, and the geometry of the ligand. We hope to exploit these factors to help control the nature of the polymers formed in a more predictable fashion.

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Supporting Information Available: Additional crystallographic data (CIF files) and ORTEP diagrams for complexes **1**–**8**. This material is free of charge via the Internet at <http://pubs.acs.org>.

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