Self assembly of silver(I) coordination polymers formed through hydrogen bonding with a new ditopic heteroscorpionate ligand†

Guillermo A. Santillan and Carl J. Carrano*

Received 26th March 2009, Accepted 29th May 2009
First published as an Advance Article on the web 2nd July 2009
DOI: 10.1039/b906047b

The new ditopic heteroscorpionate ligand, (3-methoxy-4-hydroxyphenyl)bis(3,5-dimethylpyrazolyl)methane (L5v), and four coordination polymers of silver Ag(I) derived therefrom, have been synthesized and characterized by X-ray diffraction, ESI-MS, IR spectroscopy and elemental analysis. The presence of different anions (*i.e.* BF_4^-, $CF_3SO_3^-$, NO_3^-, or SbF_6^-) lead to different crystal packing schemes due to different H-bonding patterns that depend on the relative charge delocalization and/or shape of the anion.

Introduction

Self assembly of flexible achiral ligands with metal binding sites has produced a wide variety of interesting solid state structures that have attracted attention because of possible applications in materials science.[1] Simple complexes of silver(I) have been extensively utilized as building blocks in this regard for the self assembly of supramolecular coordination polymers of differing dimensionality.[2] These polymers are of interest not only because of their remarkable molecular structures but also as a result of their potential application as gas adsorption,[3] antimicrobial,[4] conductive material,[5] luminescent,[6] and magnetic materials.[7]

In these systems extensive use has been made of the extremely strong preference displayed by silver(I) towards coordination to aromatic nitrogen donors over those of the harder oxygen ligands. Thus the synthesis and reactivity of silver(I) with nitrogen heterocyclic ligands has been extensively investigated.[8] Particularly relevant is the extensive chemistry of silver with different bis(pyrazolyl)borates and methanes in which the silver atoms are invariably coordinated solely through nitrogen pyrazoles of the ligand.[9]

While most higher order solid-state structures based on coordination polymers utilize stable coordinate covalent bonds,[10] a variety of different non-covalent interactions such as hydrogen bonding and π–π stacking can also be employed to this end.[11] Of these the hydrogen bond is the strongest, most selective and directional of these non-covalent interactions and thus potentially an effective organizing interaction for designing and controlling solid-state structures.[12] In particular amino and hydroxyl groups can be employed as linking units between two coordination monomers because of their strong tendency towards the formation of hydrogen bonds with their complement.[13] Our approach has been to make use of ditopic heteroscorpionate ligands, created by modifications to the original facially coordinate tripodal scorpionate and heteroscorpionate parents to produce different coordination polymers.[14]

Thus in previous work,[15] we have shown that 3- and 4-substituted carboxyphenyl heteroscorpionates (designated L4c and L3c) coordinate silver(I) only through the pyrazole nitrogens of the ligand leaving the uncoordinated carboxylic group free to engage in self-complementary hydrogen bonding (Fig. 1: I or II) that leads to a variety of solid-state polymers stabilized by these interactions. To establish the generality of this approach, herein we describe the preparation and crystal structure of a new heteroscorpionate ligand (L5v) whose 4-hydroxy-3-methoxy substitution is expected to lead to analogous self complimentary H-bonded interactions in the solid-state (Fig. 1: III or IV). This expectation is only partially realized and we discuss the influence of the counteranion on the intermolecular interactions and solid-state structures.

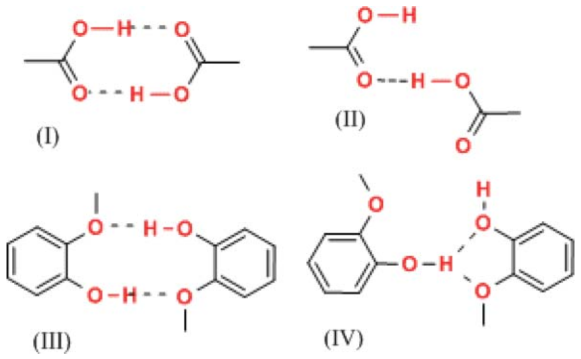


Fig. 1 Possible self-complementary hydrogen bonding.

Experimental

Materials

All chemicals and solvents used during these syntheses were reagents grade. Bis(3,5-dimethylpyrazolyl)ketone was prepared according to the procedure described by Thé and Peterson.[16]

Department of Chemistry and Biochemistry, San Diego State University, San Diego, CA 92182-1030. E-mail: carrano@sciences.sdsu.edu

† Electronic supplementary information (ESI) available: Crystal structure showing the silver–pi arene distance interaction. CCDC reference numbers 720110–720114. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b906047b

Ligand synthesis

(3-Methoxy-4-hydroxyphenyl)bis(3,5-dimethylpyrazolyl) methane (L5v). Bis(3,5-dimethylpyrazolyl)ketone (2.4 g, 11 mmol) was placed in a 100 cm^3 round-bottomed flask. 4-Hydroxy-3-methoxybenzaldehyde (1.62 g, 10.8 mmol), $CoCl_2$ (20 mg) and triethylamine (4 mL) were then added. The mixture was heated to 110 °C for 4 h with vigorous stirring during which time the mixture turned deep purple and evolved CO_2. The flask was then allowed to cool to room temperature and the solid taken up in water and filtered. The filtrate was neutralized with 6 M hydrochloric acid. At *ca.* pH = 9.3 a pale brown solid began to precipitate. This solid was collected by filtration, washed with water and dried in vacuum. Yield: 68%. Anal. Calcd (Found) for L5v·H_2O, $C_{18}H_{24}N_4O_3$: C, 62.77 (62.76); H, 7.02 (7.70); N, 16.27 (16.17). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.20 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 3.76 (s, 3H, CH_3), 5.85 (s, 2H, PzH), 6.38 (q, 1H, J = 7.8 Hz, ArH), 7.56 (s, 1H, CH), 6.47 (d, 1H, J = 7.7 Hz, ArH), 6.84 (d, 1H, J = 7.6 Hz, ArH). ^{13}C NMR ($CDCl_3$) δ: 148.24, 146.65, 145.81, 141.07, 128.59, 120.08, 114.29, 109.71, 106.82, 73.92, 55.96, 13.72, 11.81. FT-IR (KBr) ν/cm^{-1}: 3519, 1558, 1530, 1464, 1392, 1250, 1223, 1128, 1034, 812, 794, 756. Melting point: 106 (1) °C.

Silver complexes

$[Ag(L5v)_2]BF_4$ (1). A tetrahydrofuran solution (4 mL) of ligand L5v (47.8 mg, 0.146 mmol) was added to a tetrahyrofuran solution (4 mL) of silver tetrafluoroborate, $AgBF_4$ (14.2 mg, 0.073 mmol), the mixture was covered with aluminium foil and stirred for 1 min. The solution was centrifuged and layered with hexanes. Colorless crystals were obtained after 2 d. Yield: 50.88 mg (82%). Anal. Calcd (Found) for $[Ag(L5v)_2]BF_4$·0.75THF, $C_{39}H_{50}N_8O_{4.75}BF_4Ag$: C, 51.96 (51.74); H, 5.59 (5.37); N, 12.43 (12.30). IR (KBr pellets) ν/cm^{-1}: 3519, 2960, 1601, 1560, 1522, 1465, 1385, 1310, 1252, 1223, 1126, 1084, 1033, 838, 812, 795, 757, 700. ESI-MS (acetonitrile): *m/z* $[Ag(L5v)_2BF_4H]^+$ = 848 amu. The same crystal packing was obtained by using silver perchlorate $AgClO_4$ in place of silver tetrafluoroborate $AgBF_4$.

$[Ag(L5v)_2]CF_3SO_3$ (2). This complex was prepared in a manner analogous to that of complex **1** using silver trifluoromethanesulfonate ($AgOSO_2CF_3$) in place of silver tetrafluoroborate ($AgBF_4$). Yield: 47.5 mg (77%). Anal. Calcd (Found) for $[Ag(L5v)_2]CF_3SO_3$, $C_{37}H_{44}N_8O_7SF_3Ag$: C, 48.85 (48.73); H, 4.88 (4.76); N, 12.32 (12.44). IR (KBr pellets) ν/cm^{-1}: 3300, 2975, 1606, 1560, 1519, 1463, 1426, 1390, 1291, 1273, 1244, 1173, 1030, 860, 839, 820, 798, 702, 636, 606.

$[Ag(L5v)_2]NO_3$ (3). The ligand L5v (22.2 mg, 0.068 mmol) was dissolved in a mixture of acetonitrile : methanol (3 mL : 1 mL) and added to a methanol solution (4 mL) of silver nitrate (5.78 mg, 0.34 mmol). The mixture was covered with aluminium foil and 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 d. Yield: 18.1 mg (64%). Anal. Calcd (Found) for $[Ag(L5v)_2]NO_3·0.25H_2O$, $C_{36}H_{44.5}N_9O_{7.25}Ag$: C, 52.27 (52.37); H, 5.42 (5.25); N, 15.24 (15.38). IR (KBr pellets) ν/cm^{-1}: 3316, 2985, 1600, 1559, 1520, 1459, 1385, 1319, 1276, 1239, 1124, 1039, 980, 856, 821, 807, 788, 702, 606.

$[Ag_2(L5v)_2](SbF_6)_2$ (4). This complex was prepared in a manner analogous to that of complex **1** using silver hexafluoroantimonate ($AgSbF_6$) in place of silver tetrafluoroborate ($AgBF_4$). Yield: 43.8 mg (69%). Anal. Calcd (Found) for $[Ag_2(L5v)_2](SbF_6)_2$·0.5THF, $C_{38}H_{48}N_8O_{4.5}Sb_2F_{12}$ Ag_2: C, 33.17 (33.35); H, 3.52 (3.71); N, 8.14 (8.32). IR (KBr pellets) ν/cm^{-1}: 3420, 1605, 1560, 1519, 1456, 1426, 1390, 1291, 1272, 1245, 1173, 1134, 1030, 860, 820, 806, 798, 779, 702, 636, 606. ESI-MS (acetonitrile): *m/z* $[Ag_2(L5v)_2SbF_6]^+$ = 1102 amu. The same crystal packing was obtained by using silver hexafluorophosphate $AgPF_6$ instead of hexafluoroantimonate $AgSbF_6$.

Physical methods

Elemental analyses were performed on all compounds by Numega laboratories, San Diego, CA. Samples were dried in vacuum prior to analysis. ^{1}H and ^{13}C NMR spectra were collected on Varian 400 and 600 MHz NMR spectrometers. Chemical shifts are reported in ppm relative to an internal standard of TMS. 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 in positive ion mode on an Agilent 6330 Series Ion Trap LC/MS system mass spectrometer equipped with an ESI source. Samples were dissolved in acetonitrile and eluted with acetonitrile containing 0.1% formic acid. Agilent 6330 Series software was used for data acquisition and plotting. Isotope distribution patterns were simulated using the program IsoPro 3.0.

X-Ray crystal structure characterization

Crystals of complexes **1–4** were mounted on nylon loops with paratone oil (Hampton Research), and placed in the cold stream (240 K) of a Bruker X8 APEX CCD diffractometer operating at 50 kV and 30 mA using Mo Kα radiation (λ = 0.71073 Å). Data for the free ligand, L5v, were collected at room temperature. 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 where noted. The relatively large residual peaks found in the final difference map of **4** are associated with the antimony of the hexafluoroantimonate anion. All software and sources of the scattering factors are contained in the SHELXTL 6.12 program library (G. Sheldrick, Siemens XRD, Madison, WI).[18] Crystallographic data for ligand L5v and silver complexes **1–4** are listed in Table 1 and selected bond lengths and angles for all compounds are given in Tables 2 and 3. CCDC reference numbers 720110–720114.†

Solid-state structure of the complexes

Silver complexes

The thermal ellipsoid diagrams for ligand (L5v) and silver complexes $[Ag(L5v)_2]BF_4$ (**1**), $[Ag(L5v)_2]CF_3SO_3$ (**2**), $[Ag(L5v)_2]NO_3$ (**3**) and $[Ag_2(L5v)_2](SbF_6)_2$ (**4**) are depicted in Fig. 2. Select bond distances and angles for complexes **1–4** are shown in Tables 2 and 3. The reaction of ditopic heteroscorpionate ligand L5v with silver tetrafluoroborate $AgBF_4$, silver triflate $AgCF_3SO_3$,

Table 1 Crystallographic data and parameters for: ligand (L5v)·H_2O, [Ag(L5v)$_2$]BF_4·THF (**1**), [Ag(L5v)$_2$]CF_3SO_3·THF (**2**), [Ag(L5v)$_2$]NO_3 (**3**) and [Ag_2(L5v)$_2$](SbF_6)$_2$·2THF(**4**)

	L5v	**1**	**2**	**3**	**4**
Molecular formula	$C_{18}H_{24}N_4O_3$	$C_{40}H_{52}N_8O_5BF_4Ag$	$C_{41}H_{52}N_8O_8SF_3Ag$	$C_{36}H_{44}N_9O_7Ag$	$C_{44}H_{58}N_8O_6F_{12}Sb_2Ag_2$
FW	344.41	919.58	981.84	822.67	1482.22
T/K	298(2)	240(2)	240(2)	240(2)	240(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$C2/c$
a/Å	7.8522(2)	9.3894(7)	12.3951(10)	9.5688(4)	15.0535(4)
b/Å	9.8917(2)	24.7239(18)	12.7251(11)	15.7555(7)	17.1969(4)
c/Å	12.2509(3)	18.8870(13)	16.9436(14)	24.7812(12)	20.9904(6)
α/°	80.3380(10)	90	77.654(3)	90	90
β/°	77.7700(10)	97.518	71.812(3)	91.724(2)	92.663(2)
γ/°	88.9180(10)	90	62.334(3)	90	90
V/Å^3	916.62(4)	4346.8(5)	2241.1(3)	3734.4(3)	5428(2)
Z	2	4	2	4	4
μ/mm^{-1}	0.087	0.532	0.568	0.600	1.789
ρ_{calc}/g cm^{-3})	1.248	1.405	1.455	1.463	1.814
F(000)	368	1904	1016	1704	2920
Size/mm^3	0.5 × 0.4 × 0.3	0.4 × 0.2 × 0.1	0.3 × 0.2 × 0.2	0.3 × 0.3 × 0.3	0.4 × 0.4 × 0.3
h, k, l ranges collected	−11 → 11 −14 → 14 −18 → 13	−10 → 11 −30 → 26 −23 → 23	−15 → 15 −16 → 16 −18 → 21	−10 → 10 −17 → 17 −27 → 27	−17 → 17 −20 → 17 −24 → 24
θ range/°	2.48–31.77	2.18–26.22	20.2–27.11	2.59–23.26	2.56–24.93
Reflections collected	21 884	42 624	41 858	33 620	48 734
Independent reflections	6243	8701	9732	5359	4737
Parameters	235	532	559	478	336
Data/parameters	26.56	16.35	17.40	11.21	14.09
$R(F)^a$	0.0886	0.0711	0.0758	0.0504	0.0517
$R_w(F^2)^b$	0.2163	0.1507	0.1319	0.1057	0.1217
GOF^c	1.052	1.015	1.027	1.027	1.032
Largest diff peak and hole/e Å^{-3}	0.422 and −0.323	0.907 and −0.719	0.658 and −0.523	0.485 and −0.334	2.196 and −1.406

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

Table 2 Selected bond lengths (Å) for: [Ag(L5v)$_2$]BF_4·THF (**1**), [Ag(L5v)$_2$]CF_3SO_3·THF (**2**), [Ag(L5v)$_2$]NO_3 (**3**) and [Ag_2(L5v)$_2$](SbF_6)$_2$·2THF (**4**)

	1	**2**	**3**	**4**
Ag(1)–N(1)	2.401(3)	2.449(3)	2.368(3)	2.138(4)
Ag(1)–N(1)#1				2.138(4)
Ag(1)–N(3)	2.260(3)	2.307(2)	2.265(3)	2.126(4)
Ag(1)–N(3)#1				2.126(4)
Ag(1)–N(5)	2.277(3)	2.385(3)	2.252(3)	
Ag(1)–N(7)	2.370(3)	2.344(3)	2.407(3)	
Ag(1)–Ag(1)#1				3.02336(7)

Table 3 Selected angles (°) for: [Ag(L5v)$_2$]BF_4·THF (**1**), [Ag(L5v)$_2$]CF_3SO_3·THF (**2**), [Ag(L5v)$_2$]NO_3 (**3**) and [Ag_2(L5v)$_2$](SbF_6)$_2$·2THF·(**4**)

	1	**2**	**3**	**4**
N(3)–Ag(1)–N(1)	82.74(10)	79.46(9)	84.09(10)	172.98(15)
N(5)–Ag(1)–N(1)	107.80(11)	159.56(9)	112.56(10)	
N(7)–Ag(1)–N(1)	107.35(10)	109.00(9)	110.40(9)	
N(5)–Ag(1)–N(3)	153.77(12)	108.49(9)	158.40(10)	
N(7)–Ag(1)–N(3)	115.41(11)	126.43(9)	104.71(10)	
N(7)–Ag(1)–N(5)	84.98(11)	81.89(9)	82.95(10)	
N(1)#1–Ag(1)–Ag(1)#1				71.29(10)
N(3)#1–Ag(1)–Ag(1)#1				107.59(10)
N(3)–Ag(1)–N(1)#1				172.98(15)

and silver nitrate $AgNO_3$ smoothly yielded complexes with a ratio of 1Ag : 2L : 1Anion. All these complexes show the same environment about the silver Ag(I) cation, which is coordinated by four pyrazole nitrogens of the chelating ligand in a pseudo-tetrahedral geometry with a structural index parameter (τ_4)[19] of 0.64 (complex **1**), 0.52 (complex **2**) and 0.63 (complex **3**). The dihedral angle between N(1)–Ag(1)–N(3) and N(5)–Ag(1)–N(7) planes are 81.88° in (**1**), 62.07° in (**2**) and 76.65° in (**3**) all of which are much closer to the 90° angle expected of a tetrahedron, than the 0° expected for the alternate square planar configuration. The largest N(3)–Ag–N(5) angles varies from 153.77° in (**1**) to 159.56° in (**2**) while that of (**3**) is intermediary at 158.40°. The remaining angles are in the range between 79.46 to 126.43°. Silver nitrogen bond lengths are asymmetric with most values falling between 2.26 and 2.44 Å.

The crystal packing architecture of (**1**) consists of self-complementary hydrogen bonding between hydroxyl groups (av. O···O 2.915 Å) leading to 1-D chains. The counteranion BF_4^- takes part in several CH···F weak hydrogen bonding interactions that support the assembly by bridging between the silver polymer chains. The CH···F interaction average is 2.55 Å (Fig. 3).

For complex **2**, as was the case for **1**, the crystal packing shows the formation of a racemic mixture of 1-D coordination polymer chiral helices (Fig. 4). However in this case they are formed, not by self-complementary hydrogen bonding between the uncoordinated hydroxyl groups, but rather through hydrogen bonding between hydroxyl groups on adjacent molecules bridged through an uncoordinated triflate counterion (av. O···O separation 2.73 Å). The helices are held together by weak π–π interactions with a distance of 3.8 Å.

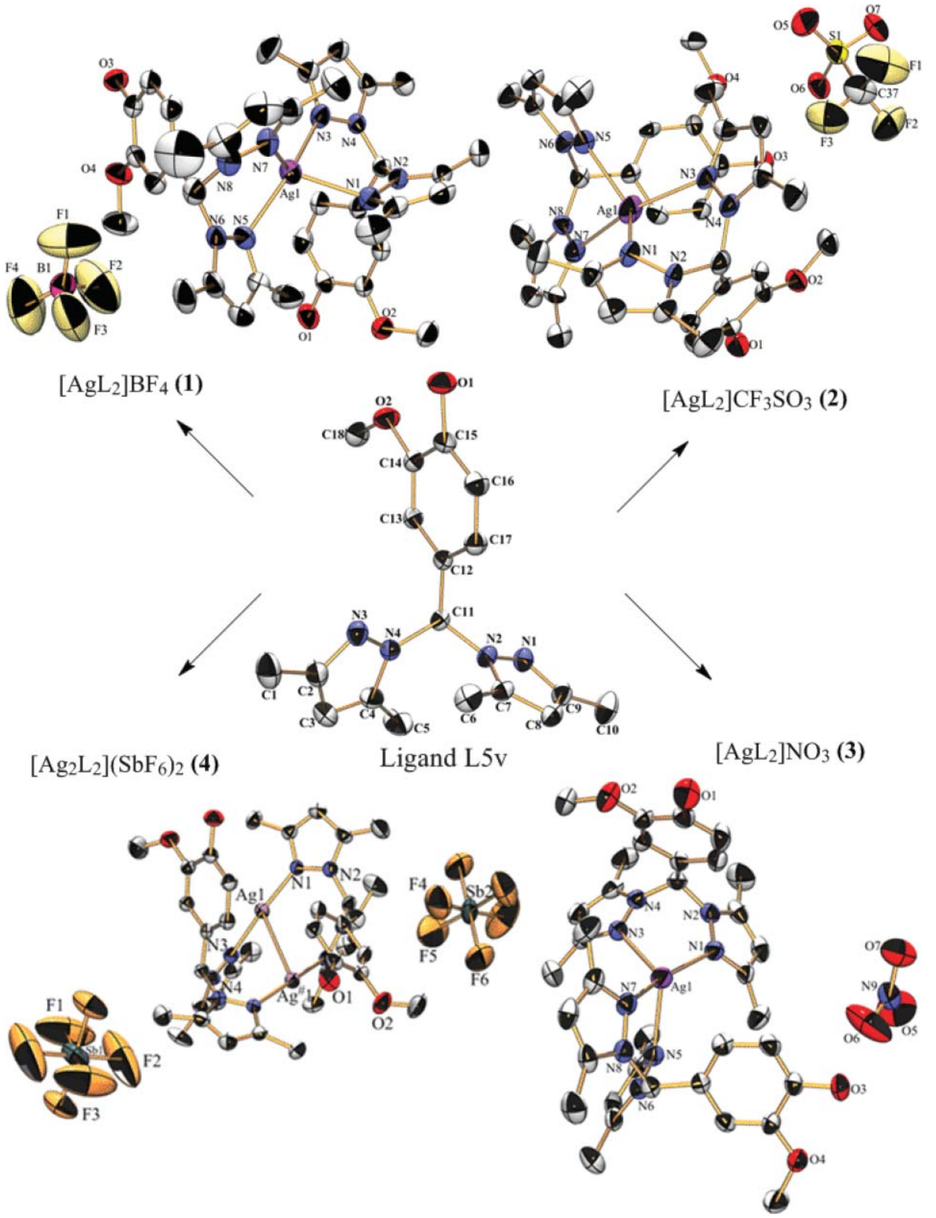


Fig. 2 Thermal ellipsoid diagram for silver complexes **1**, **2**, **3**, **4** and ligand **L5v** at the 50% probability level.

The crystal packing in **3** (Fig. 5) reveals yet a third motif where the silver monomers are linked by hydrogen bonds between the hydroxyl groups and the bridging nitrate anion to produce solid-state dimers. These dimers are also held together by weak hydrogen bonding between the methyl group C–H and the oxygen from the methoxy group (av. 3.15 Å).

The reaction of ditopic heteroscorpionate ligand L5v with silver hexafluoroantimonate $AgSbF_6$ in tetrahydrofuran produced complex **4** which is completely different from all the other complexes isolated in this study in that a 1Ag : 1L rather than a 1Ag : 2L stoichiometry is seen. Compound **4** crystallizes in space group *C*2/*c* and displays crystallographic inversion symmetry. The structure determination reveals the presence of discrete dimeric species $[Ag_2L_2](SbF_6)_2$ as depicted in Fig. 2. Each silver is equatorially surrounded by two pyrazole nitrogens, one each from two different L5v ligands. The silver atoms exhibit a distorted linear coordination with a N(1)–Ag(1)–N(3) angle of 173.2°. The silver atom separation is 3.023 Å, less that the sum of silver–silver van der Waals radii (3.44 Å), indicative of a weak Ag–Ag interaction.[21] The bridging Ag–Ag bonding is interesting and unusual for poly(pyrazolyl)methane type ligands.[22] The Ag–N bond distances are symmetrical at 2.13 Å. This complex exhibits cation–π interaction (Ag-centroid distance 3.2 Å) between the silver and aromatic ring of the ligand.

The crystal packing architecture of **4** reveals that the counteranion SbF_6^- takes part in a series of C–H···F hydrogen bonding interactions that support the assembly by bridging between the dinuclear complexes. The C–H···F "bond" distances is in the range of 2.48 Å. In addition to the interactions between the anions and the silver complex, there is also hydrogen bonding between the hydroxyl group of the ligand and a tetrahydrofuran of solvation, but these hydrogen bonds do not contribute to the development

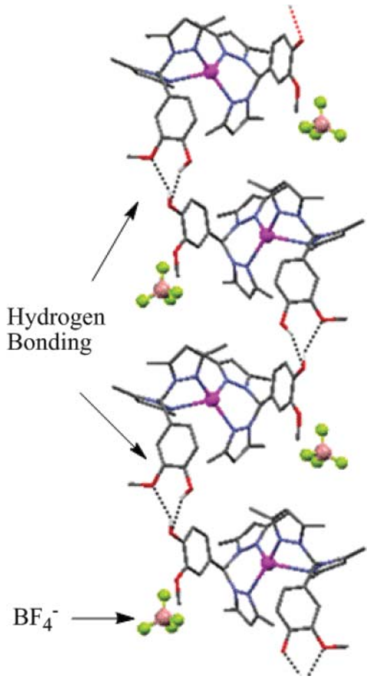


Fig. 3 Crystal packing diagram for (**1**) as seen along crystallographic *a* axis. Hydrogen bonding bonds (O···H···O and CH···F) are shown as dotted lines. Solvent molecules are omitted.

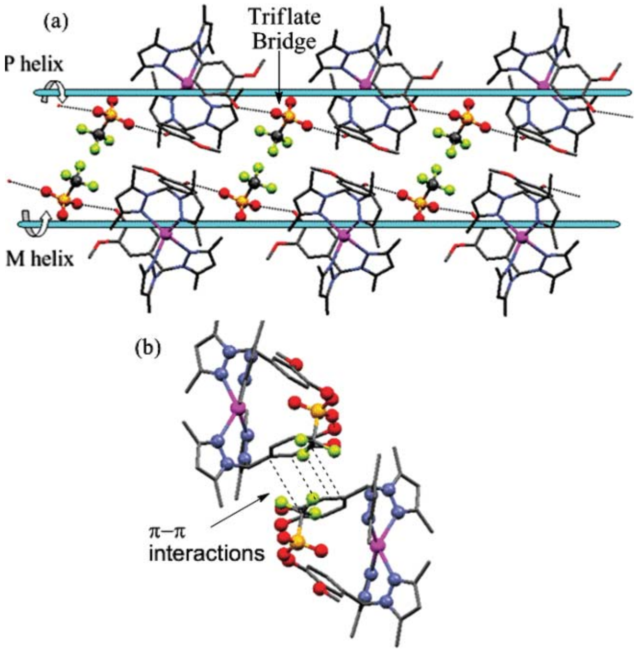


Fig. 4 (a) Crystal packing diagram for **2** showing the two chiral helices. Hydrogen bonds (O–H···O) are shown as dotted lines. (b) Crystal packing diagram for two molecules of **2** as seen along the crystallographic *a* axis; π–π interactions are shown as dotted lines. Solvent molecules and hydrogen atoms are omitted for clarity.

of a coordination polymer (Fig. 6). Indeed the hydrogen bonding by the THF of solvation serves to "cap" the free hydroxyl groups and prevents them from forming the self-complementary hydrogen bonding seen in **1**.

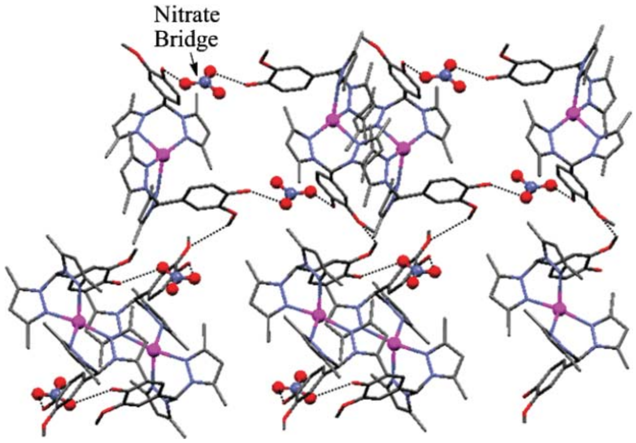


Fig. 5 Crystal packing diagram for (**3**) as seen along crystallographic *a* axis. Hydrogen bonding bonds (O···H···O and CH···O) are shown as dotted lines.

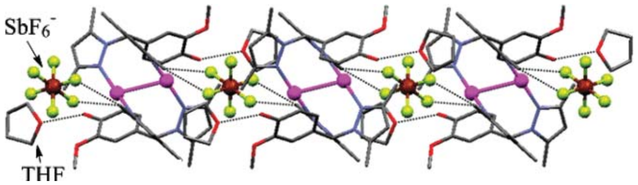


Fig. 6 Crystal packing diagram for (**4**) as seen along crystallographic *b* axis. Hydrogen bonds (O···H···O and CH···F) are shown as dotted lines.

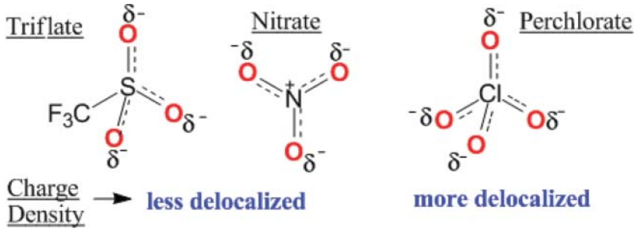
Results and discussion

Synthesis and characterization

In previous work,[15] we showed that Ag(I) binds the ditopic heteroscorpionates L4c and L3c exclusively through the softer pyrazole nitrogen donors of the ligand, leaving the carboxylic acid group uncoordinated and thus free to link the monomeric units together *via* self-complementary hydrogen bonding interactions or hydrogen bonding with solvent molecules or counter ions. In this study, we sought to determine if such a strategy was general by changing the hydrogen bonding functional group from a carboxylic acid to a 4-hydroxy-3-methoxyphenyl moiety. The reaction of the ditopic heteroscorpionate ligand designated L5v with silver Ag(I) did indeed produce coordination polymers either by self-complementary hydrogen bonding between the hydroxymethoxy moieties or *via* their hydrogen bonding with bridging anions. Thus, the reaction of the ligand L5v with silver tetrafluoroborate ($AgBF_4$) in tetrahydrofuran solvent, the polymer isolated has a [1Ag : 2L : 1BF_4] ratio where the free hydroxyl group of the ligand engages in intermolecular self-complementary hydrogen bonding to yield a 1-D coordination polymer. On the other hand the use of $AgCF_3SO_3$ as a starting material results in a product with similar stoichiometry but the anion triflate bridges between free hydroxyl groups of the chelating ligands between adjacent molecules leading to a racemic mixture of chiral linear coordination polymers. In methanol, the reaction of ligand L5v with silver nitrate $AgNO_3$ as a metal source also leads to (1M : 2L : 1Anion) stoichiometry but with the formation of solid-state dimers where the nitrate anion (NO_3^-) bridges between hydroxyl groups. The situation is different however when silver hexafluoroantimonate ($AgSbF_6$) is used in tetrahydrofuran where discrete molecular dimers of [2M : 2L : $2SbF_6$] stoichiometry are obtained.

Anion bridging

In our research, we have repeatedly observed that the anions nitrate, NO_3^-, and triflate, $CF_3SO_3^-$, behave significantly different than anions such as perchlorate (ClO_4^-), tetrafluoroborate (BF_4^-), hexafluoroantimonate (SbF_6^-) *etc.* in that they invariably form hydrogen bonds that bridge between the carboxylic acid or hydroxyl groups in the solid-state. That is they tend to break up the strong self-complementary hydrogen bonding between these groups found with the non-bonding spherically symmetric anions. To date only a few examples of nitrate and triflate anion bridging *via* hydrogen bonding are known.[20] This interaction implies that the nitrate or triflate hydrogen bonding with the carboxylate or hydroxyl centers is stronger than that provided by the corresponding ligand based self-complementary. We attribute this tendency to a difference in the charge density among the various anions where the negative charge in nitrate and triflate is less delocalized compared to non-bonding spherical anions such as perchlorate (ClO_4^-), tetrafluoroborate (BF_4^-) or hexafluoroantimonate (SbF_6^-) (Scheme 1).



Scheme 1 Representation of anions with delocalized charge.

This tendency is well illustrated in our previous work,[17] where we showed that a meso-helical solid-state polymer was formed *via* self-complementary hydrogen bonding between carboxylate groups in a Ni(II) complex with the carboxylate ligand L4c in the presence of perchlorate. However in the presence of nitrate, although a helical polymer was still produced, the nitrate ion disrupted the self-complementarity between ligands and bridged between the carboxylate units in the solid-state (Fig. 7, top). A similar situation occurs with the new L5v ligand with Ag(I) as the cation. Again in the presence of spherically symmetric anions a 1-D solid-state polymer chain is produced by self-complementary hydrogen bonding while in the presence of triflate the ligand–ligand hydrogen bonding is broken and the interaction replaced by hydrogen bonding between the bridging anion and the ligand functional group (Fig. 7, bottom). We have found many other examples of this, thus it seems to be a representative phenomenon.

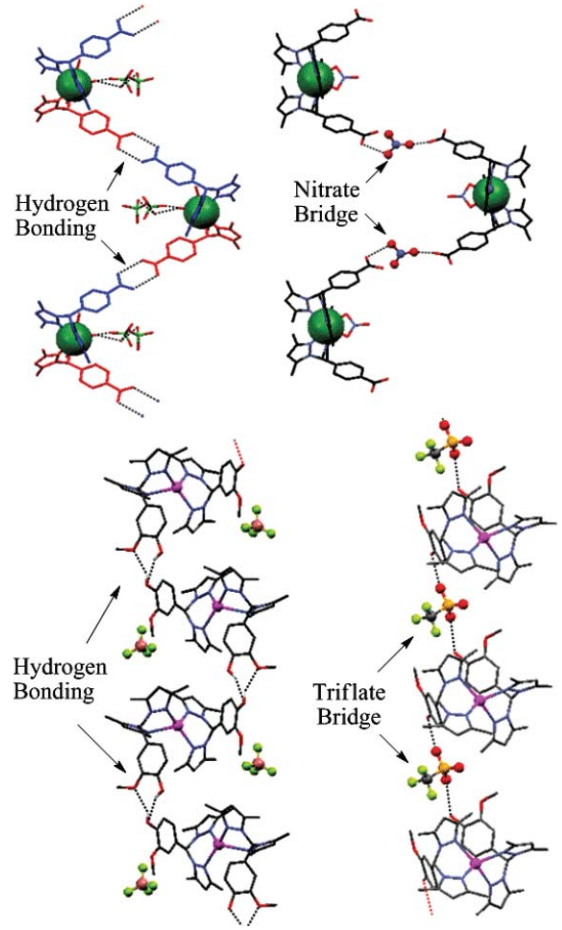


Fig. 7 Left: representation of the solid-state polymers produced by self-complementary hydrogen bonding between L4c ligands in a Ni(II) complex (upper) and L5v ligands in a Ag(I) complex (lower) with spherical anions such as perchlorate or tetrafluoroborate. Right: representation of the corresponding solid-state polymers produced with the non-spherical triflate or nitrate showing insertion of the anions between the ligands.

Conclusion

The silver(I) chemistry with the ditopic heteroscorpionate ligand L5v in the solid-state has been explored. This ligand has demonstrated the ability to yield a series of new silver complex derivatives showing both discrete and polymeric architectures. This flexible bidentate ligand is bound asymmetrically to the silver cation, producing chiral silver monomers (tectons) and leaving hydroxyl groups uncoordinated, free to engage in intermolecular hydrogen bonding. However the resulting packing contains alternating chiral monomers forming an overall racemic mixture. Moreover, the shape and size of the counteranions play an important role and dictate the crystal packing of these silver complexes. Future work will involve the demethylation of the L5v ligand to obtain the potentially "bis-bidentate" catecholate heteroscorpionate ligand.

Acknowledgements

This work was supported in part by NSF Grant CHE-0313865. The NSF-MRI program Grant CHE-0320848 is also gratefully acknowledged for support of the X-ray diffraction facilities at San Diego State University.

Notes and references

1 (*a*) C. Piguet, M. Borkovec, J. Hamacek and K. Zeckert, *Coord. Chem. Rev.*, 2005, **249**, 705–726; (*b*) M. J. Hannon and L. Childs, *J. Supramol. Chem.*, 2004, **16**, 7–22; (*c*) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005–2062; (*d*) D. S. Lawrence, T. Jiang and M. Levett, *Chem. Rev.*, 1995, **95**, 2229–2260; (*e*) L. Carlucci,

G. Ciani, D. W. Van Gudenberg and D. M. Proserpio, *Inorg. Chem.*, 1997, **36**, 3812–3813; (*f*) D. N. Dybtsev, A. L. Nuzhdin, H. Chun, K. P. Bryliakov, E. P. Talsi, V. P. Fedin and K. Kim, *Angew. Chem., Int. Ed.*, 2006, **45**, 916–920; (*g*) A. Jouaiti, M. W. Hosseini, N. Kyritsakas, P. Grosshans and J. M. Planeix, *Chem. Commun.*, 2006, 3078–3080; (*h*) P. L. Caradoc-Davies and L. R. Hanton, *Chem. Commun.*, 2001, 1098–1099.

2 (*a*) C.-L. Chen, B.-S. Kang and C.-Y. Su, *Aust. J. Chem.*, 2006, **59**, 3–18; (*b*) A. N. Khlobystov, A. J. Blake, N. R. Champness, D. A. Lemenovskii, A. G. Majouga, N. V. Zyk and M. Schroder, *Coord. Chem. Rev.*, 2001, **222**, 155–192.

3 (*a*) J. P. Zhang and S. Kitagawa, *J. Am. Chem. Soc.*, 2008, **130**, 907–917; (*b*) S. Uchida, R. Kawamoto, H. Tagami, Y. Nakagawa and N. Mizuno, *J. Am. Chem. Soc.*, 2008, **130**, 12370–12376; (*c*) C. Yang, X. Wang and M. A. Omary, *J. Am. Chem. Soc.*, 2007, **129**, 15454–15455.

4 (*a*) A. Kascatan-Nebioglu, M. J. Panzner, C. A. Tessier, C. L. Cannon and W. Youngs, *J. Coord. Chem. Rev.*, 2007, **251**, 884–895; (*b*) N. C. Kasuga, A. Sugie and K. Nomiya, *Dalton Trans.*, 2004, 3732 and references therein.

5 (*a*) P. Lin, R. A. Henderson, R. W. Harrington, W. Clegg, C.-D. Wu and X.-T. Wu, *Inorg. Chem.*, 2004, **431**, 181–188; (*b*) R. B. Fu, S. Q. Xia, S. C. Xiang, S.-M. Hu and X.-T. Wu, *J. Solid State Chem.*, 2004, **177**, 4626.

6 (*a*) Y.-L. Wang, Q.-Y. Liu and L. Xu, *CrystEngComm*, 2008, **10**, 1667–1673; (*b*) S. M. Zhang, T. L. Hu, J. R. Li, J.-L. Du and X.-H. Bu, *CrystEngComm*, 2008, **10**, 1595–1604; (*c*) C. Seward, W.-L. Jia, R.-Y. Wang, G. D. Enright and S. Wang, *Angew. Chem., Int. Ed.*, 2004, **43**, 2933; (*d*) Y. Wang, B. Ding, P. Cheng, D.-Z. Liao and S.-P. Yan, *Inorg. Chem.*, 2007, **46**, 2002–2010; (*e*) Y.-B. Dong, P. Wang, R.-Q. Huang and M. D. Smith, *Inorg. Chem.*, 2004, **43**, 4727–4739.

7 S. Yamada, T. Ishida and T. Nogami, *Dalton Trans.*, 2004, 898–903.

8 (*a*) E. C. Constable, C. E. Housecroft, M. Neuburger, S. Reymann and S. Schaffner, *CrystEngComm*, 2008, **10**, 991; (*b*) M. Oh, C. L. Stern and C. A. Mirkin, *Chem. Commun.*, 2004, 2684; (*c*) A. J. Blake, N. R. Champness, P. A. Cooke and J. E. B. Nicolson, *Chem. Commun.*, 2000, 665; (*d*) K. S. Min and M. P. Suh, *J. Am. Chem. Soc.*, 2000, **122**, 6834; (*e*) C. Seward, J. Chan, D. Song and S. Wang, *Inorg. Chem.*, 2003, **42**, 1112.

9 (*a*) D. L. Reger, E. A. Foley and M. D. Smith, *Inorg. Chem.*, 2009, **48**, 936–945; (*b*) D. L. Reger, E. A. Foley, R. F. Semeniuc and M. D. Smith, *Inorg. Chem.*, 2007, **46**, 11345–11355; (*c*) D. L. Reger, R. F. Semeniuc, V. Rassolov and M. D. Smith, *Inorg. Chem.*, 2004, **43**, 537–554; (*d*) D. L. Reger, J. R. Gardinier and M. D. Smith, *Inorg. Chem.*, 2004, **43**, 3825–3832; (*e*) D. L. Reger, R. P. Watson and M. D. Smith, *Inorg. Chem.*, 2006, **45**, 10077–10087; (*f*) D. L. Reger, R. P. Watson, J. R. Gardinier and M. D. Smith, *Inorg. Chem.*, 2004, **43**, 6609–6619; (*g*) M. J. Calhorda, P. J. Costa, O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, M. Naranjo, S. Quintal, Y.-J. Shi and M. D. Villacampa, *Dalton Trans.*, 2006, 4104–4113; (*h*) H. V. R. Dias and X. Wang, *Dalton Trans.*, 2005, 2985–2987; (*i*) M. Pellei, S. Alidori, G. Papini, G. G. Lobbia, J. D. Gorden, H. V. R. Dias and C. Santini, *Dalton Trans.*, 2007, 4845–4853.

10 (*a*) A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127; (*b*) B.-H. Ye, M.-L. Tong and X.-M. Chen, *Coord. Chem. Rev.*, 2005, **249**, 545; (*c*) B. J. Holliday and C. A. Mirkin, *Angew. Chem., Int. Ed.*, 2001, **40**, 2022–2043; (*d*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629–1658; (*e*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853–908; (*f*) G. F. Swiegers and T. J. Malefetse, *Chem. Rev.*, 2000, **100**, 3483–3538; (*g*) M. W. Hosseini, *Acc. Chem. Res.*, 2005, **38**, 313–323; (*h*) A. Y. Robin and K. M. Fromm, *Coord. Chem. Rev.*, 2006, **250**, 2127–2157.

11 (*a*) H. W. Roesky and M. Andruh, *Coord. Chem. Rev.*, 2003, **236**, 91–119; (*b*) C. J. Janiak, *J. Chem. Soc., Dalton Trans.*, 2000, 3885–3896 and references therein.

12 (*a*) T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48–76; (*b*) D. Braga and F. Grepioni, *Acc. Chem. Res.*, 2000, **33**, 601–608; (*c*) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375–1406; (*d*) S. Kitagawa and K. Uemura, *Chem. Soc. Rev.*, 2005, **34**, 109–119.

13 (*a*) S. Bianketti, A. J. Blake, C. Wilson, P. Hubberstey, N. R. Champness and M. Schroder, *CrystEngComm*, 2009, **11**, 763–769; (*b*) D. Braga, S. L. Giaffreda, F. Grepioni, L. Maini and M. Polito, *Coord. Chem. Rev.*, 2006, **250**, 1267–1285; (*c*) A. M. Beatty, *CrystEngComm*, 2001, **3**, 243–255; (*d*) A. J. Blake, P. Hubberstey, U. Suksangpanya and C. L. Wilson, *J. Chem. Soc., Dalton Trans.*, 2000, 3873–3880; (*e*) A. N. Khlobystov, M. T. Brett, A. J. Blake, N. R. Champness, P. M. W. Gill, D. P. O'Neill, S. J. Teat, C. Wilson and M. Schroder, *J. Am. Chem. Soc.*, 2003, **125**, 6753–6761.

14 (*a*) S. Trofimenko, *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*, Imperial College Press, London, UK, 1999; (*b*) A. Otero, J. F. B. Antiñolo, J. Tejeda and A. Lara-Sánchez, *Dalton Trans.*, 2004, 1499–1510.

15 G. A. Santillan and C. J. Carrano, *Cryst. Growth Des.*, 2009, **9**, 1590–1598.

16 K. I. Thé and L. K. Peterson, *Can. J. Chem.*, 1973, **51**, 422.

17 G. A. Santillan and C. J. Carrano, *Dalton Trans.*, 2008, 3995–4005.

18 (*a*) *Bruker AXS Inc. APEXII software, Version 6.12*, Bruker AXS Inc., Madison, Wisconsin, USA, 2004; (*b*) G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.

19 L. Yang, D. R. Powell and R. P. Houser, *Dalton Trans.*, 2007, 955–964.

20 (*a*) D. A. McMorran, *Inorg. Chem.*, 2008, **47**, 592–601; (*b*) C. B. Aakeroy and A. M. Beatty, *J. Mol. Struct.*, 1998, **474**, 91; (*c*) D. L. Reger, E. A. Foley, R. F. Semeniuc and M. D. Smith, *Inorg. Chem.*, 2007, **46**, 11345–11355.

21 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

22 D. L. Reger, R. F. Semeniuc and M. D. Smith, *Dalton Trans.*, 2008, 2253–2260.