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Structural Variations in Novel Silver(I) Complexes with Bitopic Pyrazole/*N*-Heterocyclic Carbene Ligands

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The synthesis and structural characterization of several new silver complexes of L (L = a bidendate ligand of pyrazole and *N*-heterocyclic carbene) are described. The result shows that the choice of counterions, *N*-substitutions of L, and reaction conditions are crucial which lead to a variety of structural motifs, including novel metallomacrocycles $[Ag_2(\mu\text{-}L)_2]^{2+}$ with or without Ag···Ag close contact, a mononuclear $[AgL_2]^+$ complex, and a $[LAg(NO_3)]_n$ coordination polymer. In particular, the nonbonding Ag···Ag distance and the overall geometry of the metallomacrocycles are controllable with different *N*-substitutions and counterions. All these complexes have been determined by X-ray diffraction. The solid-state aggregates are retained in solution as supported by the electrospray mass spectroscopic studies.

Introduction

N-Heterocyclic carbenes (NHCs) have attracted much attention because their transition metal complexes display rich coordination chemistry and have wide applicability in catalysis.[1] Recently, research efforts have also been devoted to the synthesis of polydentate ligands containing NHC moieties. For example, the combination of pyridine and NHC functionalities leads to diverse polydentate ligands, some of which have shown interesting coordination chemistry,[2−5] efficient catalytic applications,[6−8] and biological activities.[9] Currently, our laboratory is also engaged in projects in which we prepare and explore the potential utilities of new polydentate ligands with NHC and other classical donors

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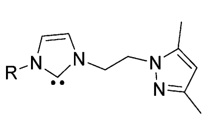
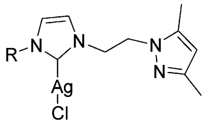
incorporated in the ligand frameworks.[10] The pyrazole/NHC ligand (L), recently prepared by in our laboratory,[11] displays interesting coordination and structural chemistry. While chelating palladium complexes of L do not form, presumably because of the intrinsic instability of the seven-member palladacycles, crystal structures of $[LH]^+Cl^-$, as well as their silver and palladium complexes, show an intriguing solid-state gauche preference in which the less-stable gauche conformation of the ethylene spacer prevails.[11] While 1:2 cationic silver NHC complexes of the type $[Ag(NHC)_2]X$ are numerous in the literature,[8e,11,12] the LAgCl complex[11] is a rare example of a neutral monomeric silver carbene of the type Ag(NHC)Cl.[2a,13] Since LAgCl still contains a free pyrazole moiety for metal coordination, it can be anticipated that preparation of novel bimetallic complexes containing bitopic L are feasible via both pyrazole and imidazole ring coordination.



L



LAgCl

Continuing with our interest in the ligand L, we describe the synthesis and structural characterization of several new silver complexes of L (Scheme 1). Our new result shows that the choice of counterions, *N*-substitutions of L, and reaction conditions are crucial and can lead to a variety of structural architectures, including novel metallomacrocycles $[Ag_2(\mu\text{-}L)_2]^{2+}$ with or without Ag···Ag close contact, a mononuclear *trans*-$[AgL_2]^+$ complex, and a $[LAg(NO_3)]_n$ coordination polymer. In particular, the nonbonding Ag···Ag distance and the overall geometry of the metallomacrocycles are controllable with different *N*-substitutions and counterions.

Experimental Section

General Procedure. All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. All solvents used were purified according to standard procedures.[14] Commercially available chemicals were purchased from Aldrich or Acros. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded at 300.13 and 75.48 MHz, respectively, on a Bruker AV-300 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in parts per million relative to the residual proton of $CDCl_3$ (^1H, δ 7.24; ^{13}C, δ 77.0) and DMSO-d_6 (^1H, δ 2.50; ^{13}C, δ 39.5). Elemental analyses and ES-MS mass spectra were performed on a Heraeus CHN-OS Rapid Elemental Analyzer and a Finnigan/Thermo Quest MAT 95XL, respectively, at the Instruments Center of National Chung Hsing University, Taiwan. The syntheses of **1b** and **1c** were carried out according to literature procedures.[11]

Preparation of 1a. Compound **1a** was prepared with a procedure similar to that of **1b** and **1c**.[11] 1-Benzyl-3-[2-(3,5-dimethylpyrazol-1-yl)ethyl]-3*H*-imidazol-1-ium chloride (0.52 g, 1.63 mmol) and Ag_2O (0.19 g, 0.819 mmol) were used. A white solid was obtained. Yield: 0.61 g (87%). Anal. Calcd for $C_{17}H_{20}N_4AgCl$: C, 48.19; H, 4.75; N, 13.22. Found: C, 48.19; H, 4.71; N, 13.19. mp: 117 °C. ^1H NMR ($CDCl_3$): δ 1.67 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 4.23 (t, $^3J_{HH} = 5.2$ Hz, 2H, CH_2), 4.50 (t, $^3J_{HH} = 5.2$ Hz, 2H, CH_2), 5.15 (s, 2H, CH_2), 5.60 (s, 1H, C*H*), 6.56 (s, 1H, imi-*H*), 6.82 (s, 1H, imi-*H*), 7.23−7.26 (m, 5H, Ph-*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 10.3 (CH_3), 13.3 (CH_3), 48.9 (CH_2), 51.4 (CH_2), 55.4 (CH_2), 105.0 (Py-*C*H), 120.9 (imi-*C*H), 122.1 (imi-*C*H), 127.5 (Ph-*C*H), 128.3 (Ph-*C*H), 128.7 (Ph-*C*H), 135.4 (Ph-*C*), 139.9 (Py-*C*), 148.4 (Py-*C*), 180.3 (Ag−*C*).

Preparation of 2b. A sample of **1b** (104 mg, 0.22 mmol) and silver nitrate (37 mg, 0.22 mmol) in 20 mL of CH_3CN was stirred at room temperature overnight. The solid formed was filtered on a frit and then redissolved in DMF. After the mixture was vigorously stirred, it was centrifuged and decanted to give a colorless solution; the solvent was removed completely under vacuum to give a white solid. Yield: 92 mg (84%). Anal. Calcd for $C_{42}H_{44}N_{10}Ag_2O_6$: C, 50.42; H, 4.43; N, 14.00. Found: C, 50.30; H, 4.41; N, 14.07. mp: 178−180 °C. ^1H NMR (DMSO-d_6): δ 1.86 (s, 6H, CH_3), 1.97 (s, 6H, CH_3), 4.61−4.63 (m, 4H, NCH_2CH_2N), 4.72−4.74 (m, 4H, NCH_2CH_2N), 5.66 (s, 4H, CH_2Np), 5.71 (s, 2H, Py-*H*), 6.84 (s, 2H, imi-*H*), 7.02 (s, 2H, imi-*H*), 7.09 (d, $^3J_{HH} = 7.2$ Hz, 2H, Np-*H*), 7.32 (t, $^3J_{HH} = 7.2$ Hz, 2H, Np-*H*), 7.42−7.45 (m, 4H, Np-*H*), 7.72−7.82 (m, 6H, Np-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 11.0 (CH_3), 14.2 (CH_3), 48.8 (CH_2), 51.3 (CH_2), 52.2 (CH_2), 106.2 (Py-*C*H), 123.4, 124.2, 125.8, 126.7, 127.1, 129.0, 129.1, 130.6, 133.3, 133.7 (Np-*C*, Np-*C*H), 143.3 (Py-*C*), 149.4 (Py-*C*), 180.2 (Ag−*C*).

Preparation of 2c. Compound **2c** was synthesized following a procedure similar to that of **2b**. Compound **1c** (100 mg, 0.23 mmol) and silver nitrate (38 mg, 0.23 mmol) were used. A white solid was obtained. Yield: 75 mg (71%). Anal. Calcd for $C_{34}H_{38}N_{10}Ag_2O_6F_2$: C, 43.61; H, 4.09; N, 14.96. Found: C, 43.70; H, 4.03; N, 14.71. mp: 245−247 °C. ^1H NMR (DMSO-d_6): δ 1.85 (s, 6H, CH_3), 1.94 (s, 6H, CH_3), 4.59 (m, 4H, NCH_2CH_2N), 4.69 (m, 4H, NCH_2CH_2N), 5.27 (s, 4H, CH_2Ph), 6.00 (s, 2H, Py-*H*), 7.12−7.18 (m, 8H, Ph-*H*), 7.59 (s, 2H, imi-*H*), 7.68 (s, 2H, imi-*H*). $^{13}C\{^1H\}$ NMR (DMSO-d_6): δ 10.8 (CH_3), 14.3 (CH_3), 49.0 (CH_2), 51.3 (CH_2), 53.4 (CH_2), 106.2 (Py-*C*H), 115.9 (d, $^2J_{C-F} = 21.5$ Hz, Ph-*C*H), 122.8 (imi-*C*H), 123.6 (imi-*C*H), 129.5 (d, $^3J_{C-F} = 8.2$ Hz, Ph-*C*H), 133.9 (Ph-*C*), 143.2 (Py-*C*), 149.3 (Py-*C*), 162.1 (d, $^1J_{C-F} = 244.1$ Hz, *C*−F), 179.5 (Ag−*C*).

Preparation of 3c. A sample of **1c** (136 mg, 0.30 mmol) and silver tetrafluoroborate (60 mg, 0.30 mmol) in 20 mL of THF was

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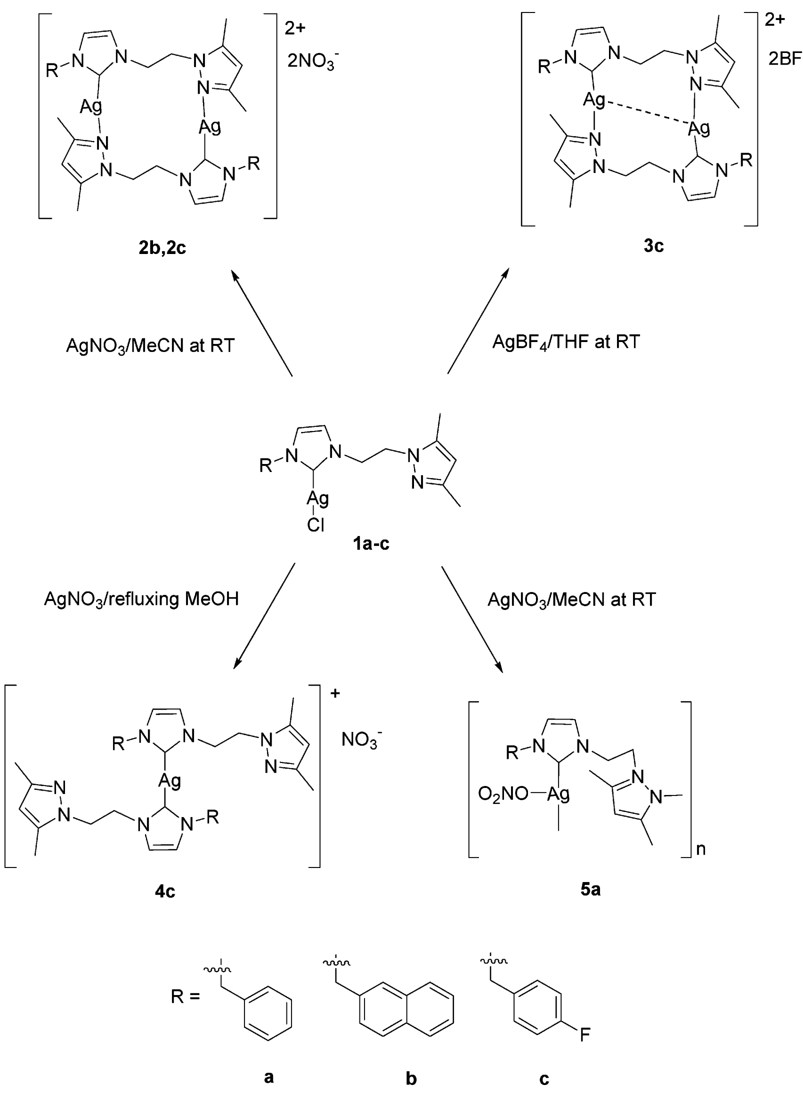
Scheme 1



stirred at room temperature for 2 h. After 10 min, a deep purple solid started to precipitate. The solid was filtered on a frit and then redissolved in DMF. After the mixture was vigorously stirred, it was centrifuged and decanted to give a colorless solution; the solvent was removed completely under vacuum to give a white solid. Yield: 109 mg (72%). Anal. Calcd for $C_{34}H_{38}B_2N_8F_{10}Ag_2$: C, 41.41; H, 3.88; N, 2.19. Found: C, 41.34; H, 3.98; N, 2.08. mp: 233−235 °C. ^{1}H NMR (DMSO-d_6): δ 1.85 (s, 6H, C*H*$_3$), 1.94 (s, 6H, C*H*$_3$), 4.56 (br s, 4H, NC*H*$_2$CH$_2$N), 4.68 (br s, 4H, NCH$_2$C*H*$_2$N), 5.26 (s, 4H, C*H*$_2$Ar), 5.99 (s, 2H, Py-*H*), 7.11−7.21 (m, 8H, Ar-*H*), 7.58 (s, 2H, imi-*H*), 7.67 (s, 2H, imi-*H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 10.7 (*C*H$_3$), 14.2 (*C*H$_3$), 49.0 (*C*H$_2$), 51.2 (*C*H$_2$), 53.4 (*C*H$_2$), 106.1 (Py-*C*H), 115.9 (d, $^2J_{C-F}$ = 21.5 Hz, Ph-*C*H), 122.8 (imi-*C*H), 123.6 (imi-*C*H), 129.5 (d, $^3J_{C-F}$ = 8.2 Hz, Ph-*C*H), 133.8 (Ph-*C*), 149.2 (Py-*C*), 143.1 (Py-*C*), 162.2 (d, $^1J_{C-F}$ = 244.1 Hz, *C*−F), 179.5 (Ag−*C*).

Preparation of 4c. A sample of **1c** (179 mg, 0.40 mmol) and silver nitrate (34.4 mg, 0.20 mmol) in 20 mL of methanol was stirred either at refluxing temperature for 4 h or at room temperature overnight. The solution was filtered through a plug of Celite. The solvent was then removed completely under vacuum to give a white compound of **4c**, which was washed several times with diethyl ether and dried under vacuum. Yield: 102 mg (67%). Anal. Calcd for $C_{34}H_{38}AgF_2N_9O_3$: C, 53.27; H, 5.00; N, 16.44. Found: C, 53.42; H, 4.95; N, 16.29. mp: 175−180 °C. ^{1}H NMR (CDCl$_3$): δ 1.75 (s, 6H, C*H*$_3$), 1.96 (s, 6H, C*H*$_3$), 4.32 (br s, 4H, NC*H*$_2$CH$_2$N), 4.63 (br s, 4H, NCH$_2$C*H*$_2$N), 5.18 (s, 4H, C*H*$_2$Ar), 5.61 (s, 2H, Py-*H*), 6.78−7.44 (m, 12H, Ar-*H*, imi-*H*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 10.4 (*C*H$_3$), 13.3 (*C*H$_3$), 48.8 (*C*H$_2$), 51.7 (*C*H$_2$), 54.4 (*C*H$_2$), 104.9 (Py-*C*H), 115.8 (d, $^2J_{C-F}$ = 21.6 Hz, Ph-*C*H), 122.8 (imi-*C*H), 122.2 (imi-*C*H), 129.0 (d, $^3J_{C-F}$ = 8.0 Hz, Ph-*C*H), 131.8 (Ph-*C*), 140.4 (Py-*C*), 148.3 (Py-*C*), 162.5 (d, $^1J_{C-F}$ = 247.8 Hz, *C*−F), 179.5 (d, $^1J_{Ag-C}$ = 191.4 Hz, Ag−*C*).

Preparation of 5a. Compound **5a** was synthesized following a procedure similar to that of **2b**. Compound **1a** (110 mg, 0.26 mmol) and silver nitrate (44 mg, 0.26 mmol) were used. A white solid was obtained. Yield: 90 mg (77%). Anal. Calcd for $C_{17}H_{20}N_5O_3$-Ag: C, 45.35; H, 4.48; N, 15.55. Found: C, 45.40; H, 4.50; N, 15.45. mp: 196−198 °C. ^{1}H NMR (DMSO-d_6): δ 1.98 (s, 6H, C*H*$_3$), 4.67 (m, 2H, NC*H*$_2$CH$_2$N), 4.76 (m, 2H, NCH$_2$C*H*$_2$N), 5.23 (s, 2H, C*H*$_2$Ph), 5.88 (s, 1H, Py-*H*), 7.03−7.04 (m, 2H, Ph-*H*), 7.27−7.30 (m, 4H, Ph-*H*, imi-*H*), 7.61 (s, 1H, imi-*H*). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 9.7 (*C*H$_3$), 13.1 (*C*H$_3$), 47.6 (*C*H$_2$), 50.0 (*C*H$_2$), 53.4 (*C*H$_2$), 104.9 (Py-*C*H), 121.0 (imi-*C*H), 121.3 (imi-*C*H), 125.8 (Ph-*C*H), 127.0 (Ph-*C*H), 127.6 (Ph-*C*H), 135.2 (Ph-*C*), 142.1 (Py-*C*), 148.5 (Py-*C*), 177.8 (Ag−*C*).

X-ray Data Collection. Crystals of **2**−**5** were obtained by vapor diffusion of diethyl ether into their corresponding DMF solutions. Typically, the crystals were removed from the vial with a small amount of mother liquor and immediately coated with silicon grease

Table 1. Crystallographic Data of **2**−**5**

	2b	**2c**	**3c**	**4c**	**5a**
empirical formula	$C_{42}H_{44}Ag_2N_8{}^{2+}$ $\cdot 2NO_3{}^- \cdot C_4H_{10}O$	$C_{34}H_{38}Ag_2F_2N_8{}^{2+}$ $\cdot 2NO_3{}^- \cdot C_3H_7NO$	$C_{34}H_{38}Ag_2F_2N_8{}^{2+}$ $\cdot 2BF_4{}^-$	$C_{34}H_{38}AgF_2N_8{}^{2+}$ $\cdot NO_3{}^- \cdot 0.25H_2O$	$C_{34}H_{40}Ag_2N_{10}O_6$
fw	1074.73	1009.58	986.08	771.11	900.50
cryst syst	monoclinic	triclinic	triclinic	triclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	30.16(2)	9.489(2)	10.8304(4)	9.4205(6)	8.8758(12)
b (Å)	8.834(5)	12.732(3)	12.2859(5)	13.4043(8)	13.9822(18)
c (Å)	18.437(11)	17.445(4)	15.4688(6)	28.8919(17)	15.222(2)
α (deg)	90	84.938(10)	97.860(2)	89.8680(10)	71.359(7)
β (deg)	107.04(2)	84.937(9)	101.205(2)	84.8040(10)	89.092(8)
γ (deg)	90	80.770(10)	105.317(2)	76.1270(10)	89.993(7)
V (Å^3)	4697(5)	2066.3(8)	1908.47(13)	3526.6(4)	1789.7(4)
T (K)	298(2)	150(2)	150(2)	150(2)	150(2)
Z	4	2	2	4	2
no. unique	5357	7809	7491	18508	6944
no. params refined	284	538	491	918	474
R1^a [$I > 2\sigma I$]	0.0638	0.0960	0.0659	0.0472	0.0970
wR2^b (all data)	0.2101	0.2531	0.1830	0.1385	0.2757

^{a} $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$. ^{b} $wR_2 = [\sum(|F_o|^2 - |F_c|^2)^2/\sum(F_o{}^2)]^{1/2}$.

on a weighting paper. A suitable crystal of each, except **2b**, was mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. A crystal of **2b** was similarly mounted and collected on a Bruker SMART 1000 CCD with the same radiation wavelength at 298(2) K at the Instruments Center, National Chung Hsing University, Taiwan. Crystallographic data for **2**−**5** are listed in Table 1.

Solution and Structure Refinements. All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods against F^2 with SHELXL-97.[15] Tables of neutral atom scattering factors, f' and f'', and absorption coefficients are from a standard source.[16] All non-hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms, except those on water, were fixed at calculated positions, and their positions were refined by a riding model.

Results

Synthesis of Metallomacrocycles 2b and 2c. The starting complex, **1**, was synthesized from reactions of the appropriate ligand precursor, $[LH]^+Cl^-$, with Ag_2O in dichloromethane as previously reported by us.[11] Since in **1**, the pyrazole ring is free of metal coordination, our initial idea was to react **1** with an equivalent amount of silver nitrate in the hope of obtaining some novel binuclear silver complexes. Therefore, we performed the initial reactions by treating **1b** and **1c** with silver nitrate in acetonitrile at room temperature. Interestingly, in both cases, a large amount of deep-colored solids were formed swiftly. Nevertheless, the mixtures were stirred for a long time to make sure that the reactions went to completion. The large amounts of solids produced suggested that a mixture of the desired product and silver chloride was formed. Hence, for product isolation, we filtered the respective solids and redissolved them in DMF. A fine powder of AgCl was removed by centrifugation, and the subsequent removal of the solvent produced the corresponding white solids of **2b** and **2c**. Both compounds are air-stable and insoluble in halogenated solvents, but they dissolve readily in high-polar solvents, such as DMSO and DMF. They are characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy as well as elemental analyses on the amorphous powders. The ^{1}H NMR spectra of **2b** and **2c** are essentially similar to those of **1b** and **1c**. The noticeable difference is that the two groups of ethylene protons in **2b** and **2c** are closer to each other ($\Delta\,\delta = \sim 0.1$) than those of **1b** and **1c** ($\Delta\,\delta = \sim 0.3$). In the ^{13}C{^{1}H} NMR spectra, the carbenic carbon signals for **2b** and **2c** were both observed at δ 179.5 as singlet, which is very close to those of their parent compounds (**1b**, δ 180.6; **1c**, δ 184.5).[11] The coupling of the carbenic carbons with silver isotopes, ^{117}Ag and ^{119}Ag, was not observed. This absence is common among Ag(NHC) complexes reported in the literature[4a,5c,11,17] and has been explained in terms of fluxional behavior.[4c,12b]

Structural Comments on 2b and 2c. To unambiguously establish the structures of **2b** and **2c**, we performed single-crystal X-ray diffraction studies. Crystals of **2b** and **2c** were obtained by vapor diffusion of a diethyl ether solution into a DMF solution containing the complexes. The structure of **2b** is solved in the monoclinic space group *C*2/*c*. As depicted in Figure 1, the structure determination reveals **2b** to be a metallomacrocycle $[Ag_2(\mu\text{-}L)_2](NO_3)_2$. The asymmetric unit consists of one-half of the molecular cation, one-half of a diethyl ether molecule, and one disordered nitrate anion. The full cation and solvent and the other nitrate anion are generated by the symmetry operation of a crystallographic 2-fold rotation axis parallel to the *b* axis. The silver center is coordinated by a NHC and a pyrazole moiety in a slightly distorted linear coordination geometry ($\angle$(C−Ag−N) = 171.1(3)°). The Ag−C bond distance of 2.078(8) Å is shorter than that of the trans Ag−N bond (2.131(6) Å), reflecting the bigger trans influence of the NHC moiety. The Ag−C bond distance is typical of other silver NHC complexes reported in the literature.[18] Intriguingly, each ethylene spacer

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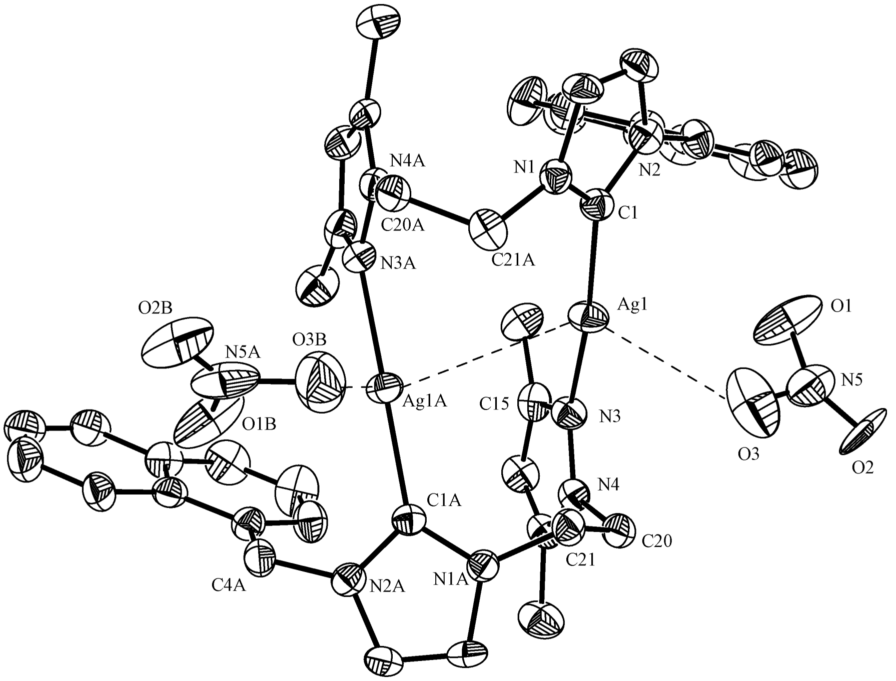

Figure 1. Thermal ellipsoid plot of **2b** at the 30% probability level. Hydrogen atoms are omitted for clarity. Only one set of oxygen atoms for the disordered nitrates are shown. Selected bond distances: Ag(1)−C(1), 2.078(8); Ag(1)−N(3), 2.131(6); Ag(1)···Ag(1A), 3.511(2) Å. Selected bond angles: C(1)−Ag(1)−N(3), 171.1(3); N(1)−C(1)−Ag(1), 131.7(6); N(2)−C(1)−Ag(1), 123.9(6); N(4)−N(3)−Ag(1), 128.3(5); C(15)−N(3)−Ag(1), 124.7(6)°.

adopts a gauche conformation (dihedral angle = 53.4(8)°) which projects the two silver ions in positions close to each other. However, the Ag···Ag distance of 3.511(2) Å is longer than the sum of van der Waals radii of two Ag atoms (3.40 Å)[19] and can be regarded as noninteracting. Each pyrazole ring is highly twisted from its trans imidazole ring with an interplanar angle of 62.8(3)°, whereas the two pyrazole rings are nearly parallel to each other (interplanar angle = 5.4(3)°). The overall geometry of the metallomacrocycle is highly twisted which can be quantified by the large C(1)−Ag(1)···Ag(1A)−N(3A) dihedral angle of 47.4(3)°. The nitrate anion in the asymmetric unit is rotationally disordered with the set of three oxygen atoms having an alternative orientation (50:50 site of occupancy). Nevertheless, this nitrate ion is interacting with the silver ion having nonbonding distances of 2.741(6)−3.182(6) Å, which are shorter than the sum of van der Waals radii for the Ag and O atoms (3.24 Å)[19] and consistent with those reported for other silver nitrate complexes in the literature.[20,21] This nitrate interaction plays a vital role in the Ag···Ag distance observed (see below, for **3c** with noncoordinating BF_4^- anions). The absence of a chloride bridge in $[Ag_3(Cl)(NO_3)(0.5DMF)(PC^{NHC}P)_2]NO_3$, in contrast to $[Ag_3(\mu\text{-}Cl)(PC^{NHC}P)_2](NO_3)_2$, was also attributed to a similar nitrate interaction present in one of the silver ions for the former complex.[10c] In $[Ag(3\text{-cyanopyridine})_2(NO_3)_3]_n$, nitrate interactions with silver ions, as well as $\pi-\pi$ stacking, contribute to its one-dimensional chain structure.[21] Unlike the solvent molecule in **2c** (vide infra), the disordered diethyl ether molecule, residing in channels along *b* axis, is not involved in any significant interactions with the cations (Figure 1S in Supporting Information).

Complex **2c** is solved in the triclinic space group $P\bar{1}$ with the asymmetric unit containing a full molecular cation, two nitrate anions, and an incorporated DMF molecule. Like **2b**, **2c** also forms a metallomacrocycle (Figure 2). The two Ag−C bonds are unequal in length (2.013(10) and 2.061(10) Å). The former distance is the shortest among silver−NHC complexes reported so far in the literature.[18] The marked differences between **2c** and **2b** are the significantly longer Ag···Ag distance of 3.852(1) Å and the more twisted geometry of the metallomacrocycle, as indicated by a larger than average C−Ag···Ag−N dihedral angle of 54.6(4)°. Each silver center is deviated from the ideal linear coordination geometry with a smaller bond angle than that of **2b** [C(1)−Ag(1)−N(8) = 165.7(4)° and C(18)−Ag(2)−N(4) = 167.8(3)°]. This can be attributed to the fact that, unlike in the structure of **2b**, one of the nitrate anions is in close contact with the silver centers of two neighboring cations (O(5)···Ag(1) = 2.955(8) Å, O(6)···Ag(1) = 3.011(7) Å, O(4)···Ag(2A) = 3.011(7) Å, and O(5)···Ag(2A) = 2.924(8) Å). These bridging nitrate interactions pull the silver centers in the metallomacrocyclic units away from each other resulting in a longer Ag···Ag distance and a one-dimensional chain structure along the *a* axis (Figure 3, top). A nitrate anion acting as a bridge between neighboring complexes is common in the literature.[20b,22] For example, a bridging nitrate anion has been observed in $[Fe(\eta^2\text{-}C_5H_4\text{-}1\text{-}C_5H_4N)_2]Ag_2(NO_3)_2\cdot 1.5H_2O$ with Ag···O distances of

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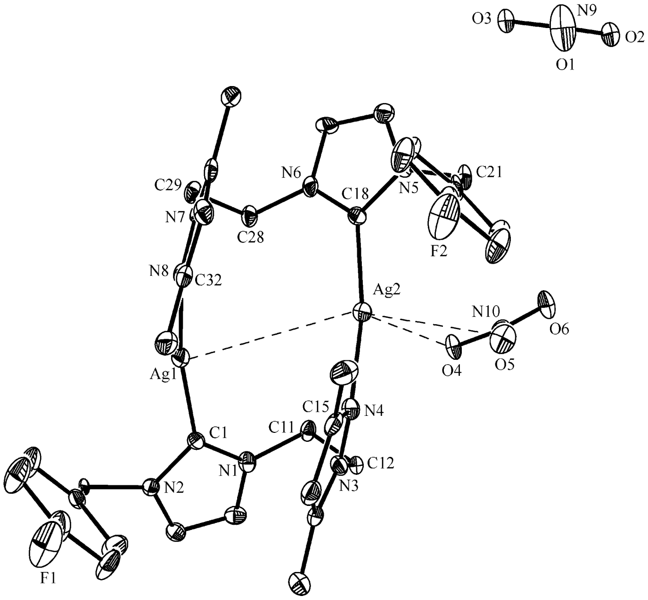

Figure 2. Thermal ellipsoid plot of **2c** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances: Ag(1)−C(1), 2.013(10); Ag(1)−N(8), 2.132(7); Ag(2)−C(18), 2.061(10); Ag(2)−N(4), 2.128(8); Ag(1)···Ag(2), 3.852(1) Å. Selected bond angles: C(1)−Ag(1)−N(8), 165.7(4); C(18)−Ag(2)−N(4), 167.8(3); N(1)−C(1)−Ag(1), 132.0(7); N(2)−C(1)−Ag(1), 127.4(7); N(7)−N(8)−Ag(1), 127.4(6); C(32)−N(8)−Ag(1), 124.5(7); N(6)−C(18)−Ag(2), 129.3(7); N(5)−C(18)−Ag(2), 127.6(7); C(15)−N(4)−Ag(2), 124.9(7); N(3)−N(4)−Ag(2), 126.0(6)°.

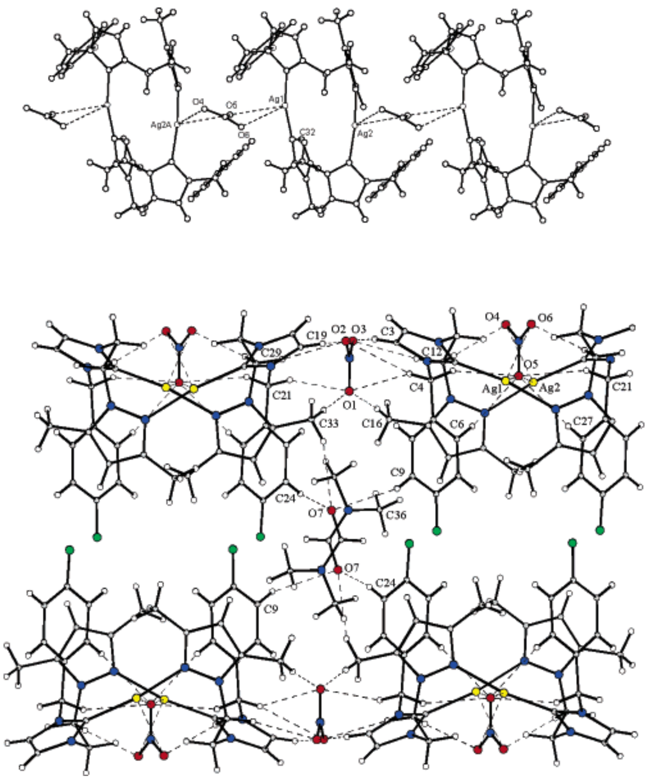

Figure 3. (top) Bridging nitrate interactions in **2c** along the *a* axis. The methyl group on C(32) is omitted for clarity. (bottom) Bilayer structure in **2c** viewed down the *a* axis. Atom colors are as follows: silver, yellow; fluorine, green; nitrogen, blue; oxygen, red; carbon, gray; hydrogen, white.

Table 2. Geometries of the C−H···O Interactions in **2c**, **4c**, and **5a**

	D−H···A	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DH···A) (deg)	symmetry code
2c	C16−H16B···O1	2.51	3.481(13)	171	$x, 1 + y, z$
	C21−H21A···O1	2.60	3.542(16)	159	x, y, z
	C4−H4A···O1	2.69	3.600(14)	152	$1 + x, 1 + y, z$
	C4−H33C···O1	2.52	3.488(12)	172	$1 + x, y, z$
	C4−H4A···O2	2.66	3.550(11)	149	$1 + x, 1 + y, z$
	C29−H29A···O2	2.61	3.566(12)	163	$1 + x, y, z$
	C3−H3···O2	2.35	3.180(13)	146	$1 + x, 1 + y, z$
	C12−H12A···O3	2.57	3.536(11)	164	$x, 1 + y, z$
	C19−H19···O3	2.31	3.160(13)	149	x, y, z
	C12−H12B···O4	2.49	3.352(14)	146	x, y, z
	C21−H21B···O5	2.54	3.405(13)	147	x, y, z
	C27−H27···O5	2.65	3.327(13)	128	x, y, z
	C6−H6···O5	2.56	3.279(14)	132	$1 + x, y, z$
	C4−H4B···O5	2.49	3.378(11)	150	$1 + x, y, z$
	C29−H29B···O6	2.50	3.376(13)	148	$1 + x, y, z$
	C24−H24···O7	2.40	3.319(14)	164	$1 - x, 1 - y, 1 - z$
	C9−H9···O7	2.56	3.344(15)	140	$1 - x, 2 - y, 1 - z$
	C33−H33···O7	2.62	3.541(13)	157	$1 - x, 2 - y, 1 - z$
4c	C29−H29A···O1	2.49	3.225(6)	154	x, y, z
	C45−H45B···O1	2.42	3.331(6)	153	$1 - x, 1 - y, 1 - z$
	C28−H28B···O2	2.57	3.482(4)	154	x, y, z
	C36−H36···O2	2.51	3.407(5)	158	$1 + x, y, z$
	C20−H20···O3	2.60	3.159(6)	118	$1 - x, 1 - y, 1 - z$
	C37−H37···O3	2.56	3.406(8)	149	$1 - x, 1- y, 1- z$
	C55−H55A···O7	2.36	3.348(8)	178	x, y, z
	C65−H65C···O7	2.52	3.430(11)	155	$1 + x, y, z$
5a	C20−H20···O1	2.42	3.231(14)	143	$1 - x, -y, -z$
	C21−H21B···O1	2.66	3.595(15)	158	$2 - x, -y, -z$
	C27−H27···O1	2.54	3.423(14)	154	$2 - x, -y, -z$
	C11−H11A···O2	2.42	3.407(12)	170	x, y, z
	C21−H21A···O2	2.62	3.444(12)	141	x, y, z
	C29−H29A···O2	2.29	3.237(12)	160	$-1 + x, y, z$
	C3−H3···O3	2.57	3.208(12)	125	$2 - x, 1 - y, -z$
	C20−H20···O4	2.57	3.208(12)	125	$1 - x, -y, -z$
	C28−H28B···O5	2.45	3.426(12)	167	x, y, z
	C4−H4B···O5	2.63	3.431(12)	139	$1 + x, y, z$
	C12−H12B···O5	2.32	3.260(12)	158	x, y, z
	C3−H3···O6	2.44	3.248(13)	143	$1 - x, 1 - y, -z$
	C4−H4A···O6	2.68	3.618(13)	158	$2 - x, 1 - y, -z$
	C6−H6···O6	2.57	3.452(15)	156	$2 - x, 1 - y, -z$

2.752(9) and 2.870(1) Å.[22b] The set of bridging nitrate anions in **2c** also involves extensive nonclassical hydrogen bonds with the aryl CH and CH_2 protons of the molecular cations (CH···O contact distances = 2.49−2.65 Å). The other set of nitrate anions form similar hydrogen-bonding interactions with the imidazolyl CH, CH_2, and CH_3 protons of the cations (CH···O contact distances = 2.31−2.69 Å), linking the one-dimensional chains into a bilayer structure in which all the fluorine atoms within the bilayer are pointing toward each other (Figure 3, bottom). The DMF solvent molecules are situated within the fluorous layer with the oxygen atom of each solvent molecule participating in trifurcated O···H−C hydrogen contacts with the aromatic CH and CH_3 donors of the molecular cations. Table 2 lists the distances and geometries of all CH···O hydrogen-bonding interactions in **2c**, which are comparable to those reported in the literature.[20d,23] For example, in $\{[Ag_2(L1)](NO_3)_2\cdot 2H_2O\}_n$ (L1 = *N*,*N*′-bis(3-pyridylmethyl)-1,4-benzenebis(methylamine)), reported by Sun et al., the nitrate anions connect 2D cationic sheets via

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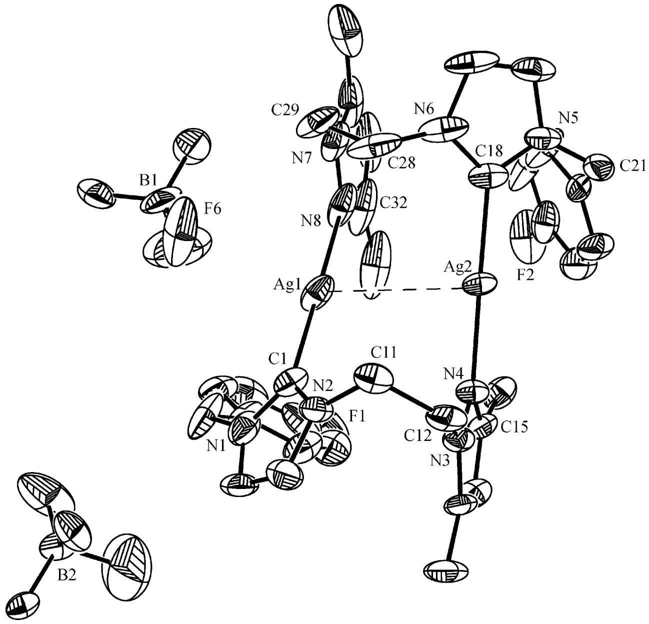

Figure 4. Thermal ellipsoid plot of **3c** at the 30% probability level. Hydrogen atoms are omitted for clarity. Only the major orientation of the disordered BF_4^- is shown (the bottom one). Selected bond distances: Ag(1)−C(1), 2.068(10); Ag(1)−N(8), 2.118(10); Ag(2)−C(18), 2.104(9); Ag(2)−N(4), 2.119(7); Ag(1)···Ag(2), 3.232(1) Å. Selected bond angles: C(1)−Ag(1)−N(8), 179.1(4); C(18)−Ag(2)−N(4), 178.5(3); N(1)−C(1)−Ag(1), 126.2(8); N(2)−C(1)−Ag(1), 129.0(8); N(7)−N(8)−Ag(1), 125.3(7); C(32)−N(8)−Ag(1), 123.6(12); N(6)−C(18)−Ag(2), 128.8(9); N(5)−C(18)−Ag(2), 125.8(7); C(15)−N(4)−Ag(2), 127.8(6); N(3)−N(4)−Ag(2), 125.9(5)°.

CH···O hydrogen-bonding interactions forming a 3D framework.[23b] The CH···O of the four hydrogen bonds involved are in the range of 2.38−2.58 Å.[23b] It should be noted that for a Ag(NHC) moiety with linear coordination geometry, the trans position is typically occupied by another NHC or a coordinated halide. Complexes **2b** and **2c** represent rare examples of an Ag(NHC) complex possessing another trans ligand.

Synthesis of Metallomacrocycle 3c. Prompted by the successful formation of metallomacrocycles from **1** and $AgNO_3$, we were interested in determining if other silver salts also mediate the formation. Hence, we carried out an initial reaction by stirring a mixture of **1c** with $AgBF_4$ in THF. In a manner similar to the reactions for **2b** and **2c**, a suspension of colored solid was produced instantaneously. A similar workup procedure was used to produce an air-stable white solid. Like **2b** and **2c**, **3c** is also insoluble in halogenated solvents. Its ^1H NMR and $^{13}C\{^1H\}$ NMR spectra are essentially identical to those of **2c**. The only noticeable difference is the slightly broadened ethylene proton signals.

Structural Comments on 3c. To probe the solid-state structure of **3c**, a suitable crystal obtained from vapor diffusion with DMF/diethyl ether solvent was analyzed at 150 K. The solid **3c** consists of a dicationic metallomacrocycle with two tetrafluoroborate anions in the asymmetric unit (Figure 4). The two Ag−C distances, like **2c**, are not equal in length (2.068(10) and 2.104(9) Å), consistent with other silver NHC complexes reported.[18] The marked differences between **2c** and **3c** are the linearity of the silver coordination environment in the latter complex (C(1)−Ag(1)−N(8) = 179.1(4)° and C(18)−Ag(2)−N(4) = 178.5(3)°) and the presence of a Ag···Ag close contact of 3.232(1) Å. The F(6) atom on one of the tetrafluoroborate anions is in the vicinity of Ag(1) with a long contact distance of 3.066(5) Å, indicating the existence of a very weak $Ag\cdots F-BF_3^-$ interaction. Hence, for compound **3c**, the negligible electrostatic interaction between the silver atom and counterion allows the predominance of an intramolecular argentophilic interaction, giving the linear coordination environment and short Ag···Ag close contact observed. In contrast, strong $Ag\cdots F-BF_3^-$ interactions were observed in $[AgL(BF_4)]_2$ (L = 1,3-bis(2-pyridylthio)propane) with a contact distance as short as 2.534 Å, which in turn produces a small N−Ag−N bond angle of 169.2(1)°.[24] Also, a salient aspect of the structure **3c** is that the extent of the macrocyclic ring twisting is the least among all three metallomacrocycles, as indicated by the smallest average C−Ag···Ag−N dihedral angle of 37.1(4)°.

Synthesis of Silver Bis(NHC) Complex 4c. Because of the instantaneous precipitation of product and AgCl in reactions between **1** and AgX (X = NO_3^-, BF_4^-) in acetonitrile at ambient temperature, it would be of interest to explore if a more polar solvent and a higher reaction temperature, which can keep the silver compound dissolved in solution, would produce the same metallomacrocycle product. Initially, we found that stirring a 1:1 molar mixture of **1c** and $AgNO_3$ in methanol at ambient or refluxing temperature produced a mixture of products as evidenced by the ^1H NMR spectroscopy. However, conducting the same reaction with a 2:1 ratio yielded only a single product. Hence, either heating or stirring a 2:1 molar mixture of **1c** and $AgNO_3$ in refluxing methanol for 4 h or in the same solvent at ambient temperature overnight produced a solution with an off-white precipitate; the small amount suggests the formation of AgCl with the desired product in solution. Therefore, the solid AgCl is filtered, and complete solvent removal from the filtrate produced an air-stable white solid. Unlike the silver compounds described above, **4c** dissolves readily in halogenated solvent. Its ^1H NMR spectrum is very similar to those of **2b**, **2c**, and **3c**. In sharp contrast, its $^{13}C\{^1H\}$ NMR spectrum exhibits coupling between the carbenic carbon and silver with a $^1J_{Ag-C}$ coupling constant of 191.4 Hz. The respective $^1J_{^{109}Ag-C}$ and $^1J_{^{107}Ag-C}$ constants were not resolved.

Structural Comments on 4c. The structure is solved in the centrosymmetric space group $P\bar{1}$. Its asymmetric unit has a full molecular cation $[AgL_2]^+$, two fragments of one-half of $[AgL_2]^+$, an incorporated water molecule with 50% site of occupancy, and two nitrate anions, one of which is disordered. The water molecule presumably originated from the wet crystallization solvents used. The geometrical data for the two independent cations at their centers of inversion are similar, and only one of these cations will be used for structural discussion. As shown in Figure 5, Ag(3), situated at an inversion center, has an ideal linear coordination geometry (C(52)−Ag(3)−C(52A) = 179.997(1)°) with the

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(24) Xie, Y.-B.; Zhang, C.; Li, J.-R.; Bu, X.-H. *Dalton Trans.* **2004**, 562.

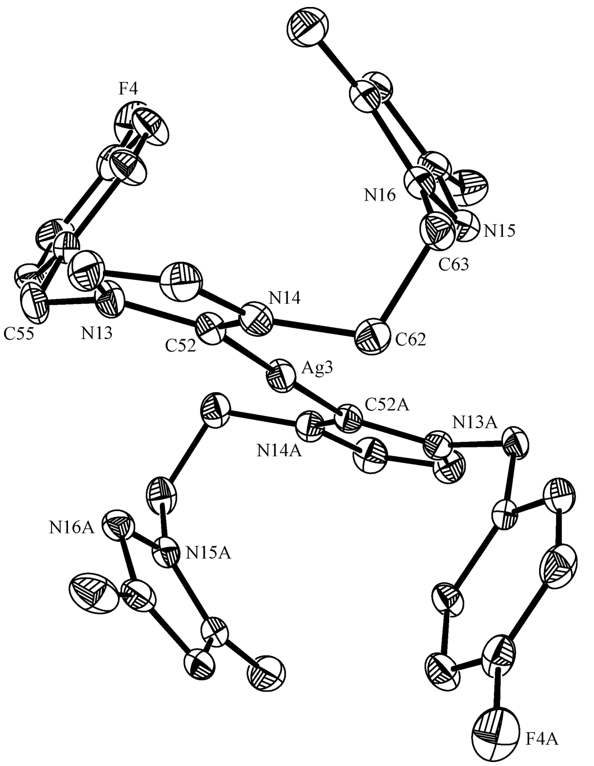

Figure 5. Thermal ellipsoid plot of the cationic portion of **4c** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances: Ag(3)−C(52), 2.079(4) Å. Selected bond angles: C(52)−Ag(3)−C(52A), 179.997(1); N(13)−C(52)−Ag(3), 127.6(3); N(14)−C(52)−Ag(3), 127.8(2)°.

two coordinating NHC rings being coplanar. The Ag(3)−C(52) distance is 2.079(4) Å, which is similar to that of other silver NHC complexes reported.[18] The four dangling arms of the two NHC rings encapsulate the silver center. Interestingly, the N(16) and N(16A) atoms of the dangling pyrazole rings are situated in positions forming a square planar geometry of the silver center with the sum of bond angles being 360°. The square-planar coordination of silver with four coordinating ligands is unusual, but it has been reported in the literature.[25] The presence of these weak interactions in **4c**, however, is dubious because of the long Ag⋯N contact distances (3.228(3)−3.401(3) Å). Interestingly, even though the geometrical data of the full molecular cation in the asymmetric unit are essentially similar to those of the two cations at centers of inversion, the coordination environment of Ag(1) is slightly deviated from the ideal 180° with C(1)−Ag(1)−C(18) = 178.03(11)°. Because the silver center is encapsulated, unlike **2b** and **2c**, there is no Ag⋯ONO_2 interaction in **4c**. The nitrate anion is solely involved in CH⋯O hydrogen-bonding interactions with the molecular cations. The distances and geometries of close contacts for the ordered nitrate anion are listed in Table 2. The incorporated water molecule is positioned about a center of inversion forming two pairs of symmetrical hydrogen bonds with O7−H7A⋯$O7^{i}$ = 2.599(9) and O7−H7B⋯$O7^{i}$ = 2.348(9) Å (symmetry code: (i) $-x$, $1 - y$, $2 - z$, Figure 2S in Supporting Information). The corresponding contact angles are 106.3(6) and 115.4(5)°, respectively. The water molecule is also involved in hydrogen-bonding interactions with the disordered nitrate anion and C(55) and C(65) of the cations. The CH⋯O interaction for C(55) is relatively strong with a contact distance of 2.36 Å and an almost linear contact angle of 178°. The corresponding distance for C(65) is 2.52 Å, with a contact angle of 155°.

Synthesis of Silver Coordinating Polymer 5a. In the starting complex **1**, the pyrazole is a free ligand moiety. The removal of coordinating chlorides from **1b** and **1c** generates a vacant silver coordination site. As a result, two molecules of this reactive species combine to form the metallomacrocycle $[Ag_2(\mu\text{-}L_2)]^{2+}$. However, it can be anticipated that the formation of a silver coordinating polymer $[AgL]_n^{n+}$ is also feasible from such reactive species. Indeed, a reaction between **1a** and $AgNO_3$ under the same reaction conditions for **2b** and **2c** produced, instead of the metallomacrocycle **2a**, a silver coordination polymer as confirmed by the X-ray structural determination (vide infra). The formation is rather surprising because the reaction was carried out under same reaction conditions and the only difference is the *N*-substitution of **1a** (R = benzyl), which is essentially similar to that of **1c** (R = 4-fluorobenzyl). The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra exhibit no significant difference from those of **2a**, **2b**, **3c**, and **4c**.

Structural Comments on 5a. Crystals suitable for X-ray diffraction studies were grown with a procedure identical to those for **2b**, **2c**, and **3c** above. It is remarkable that complex **5a**, unlike **2b**, **2c**, and **3c**, is a coordination polymer in the solid state (Figure 6). An asymmetric unit of its triclinic unit cell contains two empirical units of $[AgL(NO_3)]$. The two Ag−C distances are 2.102(10) and 2.119(10) Å, which are relatively long in comparison with the other complexes described above. Each of the two silver ions is in a highly distorted linear coordination geometry (C(1)−Ag(1)−N(8A) = 152.5(4)° and C(18)−Ag(2)−N(4) = 153.1(4)°). The distortions can be attributed to the nitrate interactions involved. The Ag(1) is chelated by the O(2) and O(3) asymmetrically with Ag⋯O nonbonding distances of 2.665(8) and 3.052(10) Å, respectively. O(2) also interacts with Ag(2) with a contact distance of 2.766(7) Å, giving a nonbonding Ag⋯Ag distance of 4.755(1) Å. The contact distance for Ag(2) with O(4) is 3.039(7) Å. Similar to O(2), O(5) is involved in bifurcated interactions with Ag(2) and an adjacent Ag(1) with contact distances of 2.660(7) and 2.770(7) Å, respectively. The six Ag⋯O nonbonding distances in the range og 2.665(8)−3.039(7) Å are typical of related silver nitrate complexes.[20,21] Ag(1) and N(8) are the points of connection linking the dimeric units into a helical polymeric chain along the *a* axis (Figure 7, top). All oxygen atoms, including the nonmetal-bonding O(1) and O(6), are involved in extensive intermolecular hydrogen contacts with the aryl CH and CH_2 protons of the molecular cations (Table 2). The CH⋯O contact distances observed are in the range of 2.29−2.68 Å, which are similar to those in **2c** and comparable with those reported in the literature.[20d,23] The metal-bonding O(2) and O(5) are involved in the two shortest CH⋯O contact distances of 2.29 and 2.32 Å. The

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[25] Arduengo, A. J., III; Rasika Dias, H. V.; Calabrese, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7071.

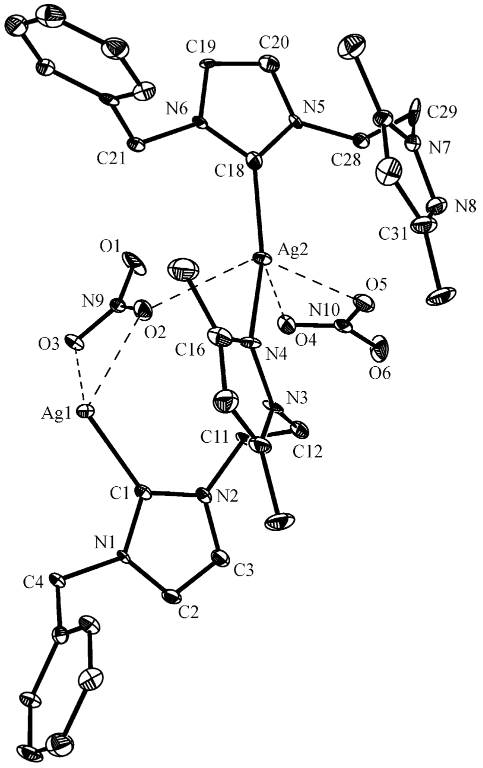

Figure 6. Thermal ellipsoid plot of **5a** at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances: Ag(1)−C(1), 2.102(10); Ag(1)−N(8A), 2.248(9); Ag(2)−C(18), 2.119(10); Ag(2)−N(4), 2.256(9) Å. Selected bond angles: C(1)−Ag(1)−N(8A), 152.5(4); C(18)−Ag(2)−N(4), 153.1(4); N(1)−C(1)−Ag(1), 126.2(7); N(2)−C(1)−Ag(1), 131.5(7); N(7)−N(8)−Ag(1A), 128.9(7); C(31)−N(8)−Ag(1A), 124.1(7); N(6)−C(18)−Ag(2), 125.7(7); N(5)−C(18)−Ag(2), 132.6(7); C(16)−N(4)−Ag(2), 124.2(7); N(3)−N(4)−Ag(2), 129.3(7)°.

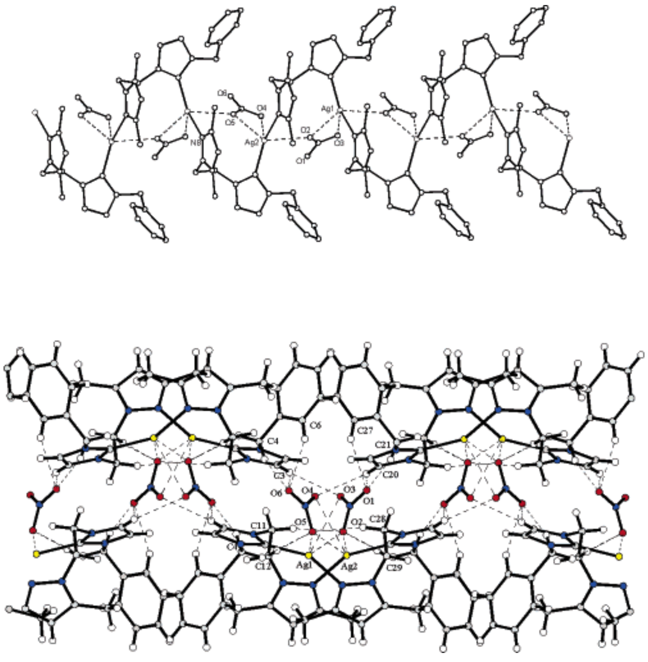

Figure 7. (top) View of a helical chain of **5a** which shows the nitrate interaction with silver atoms. (bottom) Bilayer structure in **5a** viewed down the *a* axis. Atom colors are as follows: silver, yellow; nitrogen, blue; oxygen, red; carbon, gray; hydrogen, white.

longer CH···O hydrogen contacts of 2.42−2.68 Å involving O(1), O(3), O(4), and O(6) link the polymeric chains into a bilayer structure, in which the nitrate ions and imidazole rings form the inner hydrophilic layers and the peripheral hydrophobic layer is made up of phenyl and pyrazole rings (Figure 7, bottom).

Electrospray Ionization Mass Spectrometry Studies (ES-MS). We further characterized all the new complexes by ES-MS to confirm if the species in solution are the same as those seen in the solid-state structures. The ES-MS spectra for all five complexes dissolved in DMF were recorded (Table 3). The spectra of **2b**, **2c**, and **3c** are very similar, and each complex exhibits only two major fragments, reflecting the stability of the complexes. In each case, the signal at the highest *m*/*z* corresponds to the binuclear species, $[Ag_2(\mu\text{-}L)_2(X)]^+$; for **2b** and **2c**, $[Ag_2(\mu\text{-}L)_2(NO_3)]^+$ are observed at *m*/*z* 938 and 874, respectively, whereas for **3c**, $[Ag_2(\mu\text{-}L)_2(BF_4)]^+$ is observed at *m*/*z* 899. The base peak in each spectrum corresponds to a species consisting of two ligands and a silver ion, $[AgL_2]^+$ (**2b**, *m*/*z* 769; **2c**, *m*/*z* 705; **3c**, *m*/*z* 705). All of the assignments are in good agreement between the observed and calculated isotopic distributions. The presence of binuclear species, $[Ag_2(\mu\text{-}L)_2X]^+$ ($X = NO_3$ and BF_4), confirm unambiguously that the metallomacrocyclic structures determined in the solid state are retained in the solution. The ES-MS spectrum of **4c** is markedly different from those of **2b**, **2c**, and **3c**. The peak at the highest *m*/*z* of 705 corresponds to $[AgL_2]^+$, whereas the base peak at *m*/*z* 405 is assignable to $[AgL]^+$. The loss of silver from $[AgL]^+$ produces $[L + H]^+$ at *m*/*z* 299. This also confirms that in **4c** the 1:2 Ag/L solid-state structure is the same as that in solution. The ES-MS spectrum of **5a** also displays signals from the $[AgL]^+$ and $[L + H]^+$ fragments at *m*/*z* 389 and 281, respectively. However, intriguingly, the anticipated signal from the monomeric species of $[AgL(NO_3) + H]^+$ at *m*/*z* 450 is not observed. Instead, a signal at *m*/*z* 461 is observed. The difference of 11 *m*/*z* suggests that it is a doubly charged species containing a sodium ion.[26] A dimeric species of $[\{LAg(NO_3)\}_2 + H + Na]^{2+}$ is consistent with this observed signal. The presence of mono- and dimeric species under the ES-MS experimental conditions strongly suggests the polymeric nature of **5a** in solution.

Discussion

The NHC moiety in a silver−NHC complex is labile and can be transferred to other metals facilely. There are numerous examples of transition metal NHC complexes, which are prepared by the silver carbene transfer reaction.[12b,c] However, for the reactions between **1a**−**1c** and AgX ($X = NO_3^-$, BF_4^-), it is plausible that they follow either a carbene transfer pathway between silver atoms or a simple metathesis reaction with precipitation of AgCl. The possibility of scrambling between these two pathways also exists. Appropriate labeling experiments will be necessary, but because of the unavailability of pure silver isotopes, the exact pathway remains ambiguous. Nevertheless, intriguing metallomacrocycles of **2b**, **2c**, and **3c** can be obtained readily in high yields.

The structural studies on **2b**, **2c**, and **3c** show that the *N*-substitutions exert a profound influence on the nonbonding

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(26) Gaskell, S. J. *J. Mass Spectrom.* **1997**, *32*, 677.

Table 3. ES Mass Spectroscopic Data for Complexes **2**−**5**

2b		**2c**		**3c**	
m/z	assignment	*m/z*	assignment	*m/z*	assignment
938 (10)	$[Ag_2(\mu\text{-}L)_2(NO_3)]^+$	874(15)	$[Ag_2(\mu\text{-}L)_2(NO_3)]^+$	899 (20)	$[Ag_2(\mu\text{-}L)_2(BF_4)]^+$
769 (100)	$[AgL_2]^+$	705(100)	$[AgL_2]^+$	705 (100)	$[AgL_2]^+$

4c		**5a**	
m/z	assignment	*m/z*	assignment
705 (40)	$[AgL_2]^+$	461 (10)	$[\{LAg(NO_3)\}_2 + H + Na]^{2+}$
405 (100)	$[AgL]^+$	389 (100)	$[AgL]^+$
299 (55)	$[L + H]^+$	281 (30)	$[L + H]^+$

Ag⋯Ag distances. In **2b**, the larger *N*-naphthylmethyl substituents do not allow nitrate-bridging interactions and result in a relatively short Ag⋯Ag distance of 3.511 Å, whereas the smaller *N*-4-fluorophenyl group in **2c** allows the formation of a bilayer structure in which the nitrate-bridging interactions projects the two silver centers out from the metallomacrocycle, producing a significant longer Ag⋯Ag distance of 3.852 Å. A comparison of the structures of **2c** and **3c** clearly shows that the noncoordinating nature of the BF_4^- anions allows the predominance of the intramolecular argentophilic interaction in **3c**, which results in the linear coordination geometry at the silver centers and the shortest Ag⋯Ag distance of 3.232 Å. In fact, a plot of the nonbonding Ag⋯Ag distances with the average bond angles in **2c**, **2b**, and **3c** exhibits a linear relationship (Figure 8a), indicating the tunable nature of the Ag⋯Ag distances by the *N*-substitutions and electrostatic interactions of the counterions. Most significantly, a similar plot of the Ag⋯Ag distances with the dihedral angles in **2c**, **2b**, and **3c** also displays a linear correlation, showing remarkable control by the Ag⋯Ag interaction on the macrocyclic ring (Figure 8b). Thus, the overall geometry of the metallomacrocycle can be precisely controlled by the type of *N*-substitution and counterion.

We have shown previously that under similar reaction conditions, $[LH]^+Cl^-$ which contains a sterically less bulky *N*-methyl substitution formed a common $[Ag(NHC)_2]^+$ type of cation, instead of Ag(NHC)Cl in the reaction between $[LH]^+Cl^-$ and Ag_2O.[11] In the present case, the formation of a similar 1:2 Ag/L complex **4c**, instead of a metallomacrocyclic complex, from the reaction between **1c** and $AgNO_3$ in methanol indicates the importance of reaction conditions on the selectivity of the final silver−NHC product as well. In fact, the most abundant peak in the ES-MS spectrum of **3c** corresponding to the highest *m*/*z* peak of $[AgL_2]^+$ for **4c** provides strong evidence that the 1:2 Ag/L complexes are thermodynamically more stable than the metallomacrocyclic compounds. However, it is rather surprising that a coordination polymer, **5a**, is formed from a reaction between **1a** and $AgNO_3$ under reaction and crystallization conditions similar to those for the metallomacrocycle products **2b**, **2c**, and **3c**. Chung et al. reported a similar finding in which silver nitrate forms a metallomacrocycle with 1,3-bis(2-pyridyl)-2-tolypropane, whereas a coordination polymer results from the structurally similar 1,3-bis(2-pyridyl)-2-phenylpropane ligand.[22a] In fact, it has been shown that various subtle factors, including solvents and anions, have significant impacts on the supramolecular structures of silver(I) complexes with flexible ligands.[23a,23b,27]

In this work, we demonstrated that a variety of structural motifs, including novel metallomacrocycles $[Ag_2(\mu\text{-}L)_2]^{2+}$, a mononuclear *trans*-$[AgL_2]^+$ complex, and a $[LAg(NO_3)]_n$ coordination polymer, can be obtained from reactions of LAgCl with silver salts. The nonbonding Ag⋯Ag distances and the geometries of the macrocyclic rings in $[Ag_2(\mu\text{-}L)_2]X_2$ can be precisely controlled by different *N*-substitutions and counterions. The ES-MS data prove unambiguously that the solid-state structures of **2**−**5** are retained in solution. All these silver complexes are very robust. In fact, solutions of **2**−**5** can stand in the air for several weeks without appreciable decomposition. This robustness is one of the

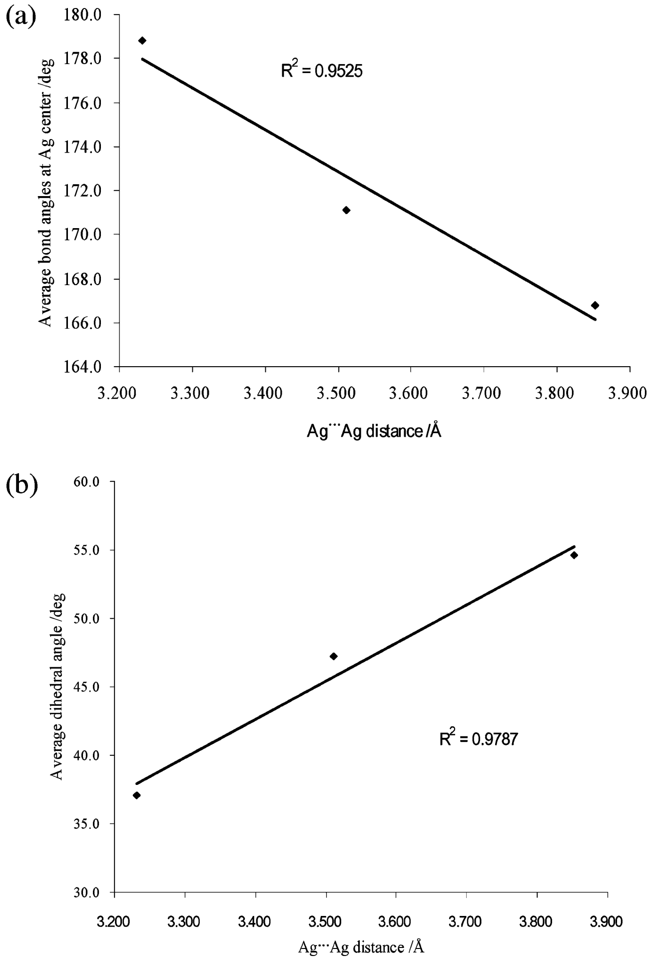

Figure 8. (a) Plot of the Ag⋯Ag distance with the average bond angles of the silver atom in **2b**, **2c**, and **3c**. (b) Plot of the Ag⋯Ag distance with the average C−Ag⋯Ag−N dihedral angle in **2b**, **2c**, and **3c**.

prerequisites in the construction of novel supramolecular molecules for materials and bioorganic applications. Further investigation with other silver salts and studies on photophysical properties are currently ongoing.

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Supporting Information Available: Full crystallographic data for compounds **2**−**5** in CIF format and packing diagrams of **2b** and **4c**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 269210−269214. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax +44(0)-1223-336033 or email deposit@ccdc.cam.ac.uk].

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