

Strained silver(I) coordination polymers of 1,4-diazatriphenylene

Farzad Haftbaradaran,^a Neil D. Draper,^a Daniel B. Leznoff^{*a} and Vance E. Williams^{*b}^a Department of Chemistry, Simon Fraser University, 8888 University Dr., Burnaby, British Columbia, Canada V5A 1S6. E-mail: dleznoff@sfu.ca; Fax: 604 291 3765; Tel: 604 291 4887^b Department of Chemistry, Simon Fraser University, 8888 University Dr., Burnaby, British Columbia, Canada V5A 1S6. E-mail: vancew@sfu.ca; Tel: 604 291 3352

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Two-dimensional coordination polymers of AgX (X = BF₄⁻, ClO₄⁻) and 1,4-diazatriphenylene show significant distortions of the polycyclic aromatic ligand and a new unsymmetrical η²-μ-η² bonding mode for BF₄⁻ and ClO₄⁻.

Silver(I)-nitrogen bonds have been used extensively to assemble coordination polymers.¹⁻⁴ Almost invariably, the ligands employed have been pyridine- or pyrazine-based systems that afford unimpeded access to the nitrogen donors. In contrast, the nitrogen atoms in 1,4-diazatriphenylene (**1**) are partially blocked by the bay hydrogens H^a and H^b (Fig. 1). This steric obstacle to coordination at the nitrogen donors is reflected in the observation that **1** acts as only a very weak hydrogen bond acceptor in solution.^{5,6} No metal complexes or coordination polymers of **1** or other similarly congested heterocyclic amines have been reported. Given this, and the propensity of Ag(I) to coordinate in an η¹ or η² fashion to the periphery of polycyclic aromatic hydrocarbons,^{7,8} the question arises as to if and how Ag(I) cations would bind to **1**.⁹

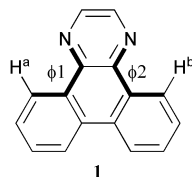


Fig. 1 Structure of 1,4-diazatriphenylene (**1**). Bold lines indicate torsional angles ϕ_1 and ϕ_2 .

To address this issue, **1** was prepared⁹ and reacted with AgBF₄, producing a yellow precipitate.† Elemental analysis indicated a compound of stoichiometry [1·AgBF₄] (**2**). The IR spectrum of **2** differs from that of **1** in that it contains extra peaks corresponding to the BF₄⁻ and a shift in the 750 cm⁻¹ band of **1** to 765 cm⁻¹. Complex **2** decomposes at 280 °C compared with 180 °C, the melting point of **1**.

The X-ray crystal structure of **2**‡ (Fig. 2) confirms the empirical formula of [1·AgBF₄] and reveals a one-dimensional coordinately bonded chain along the *b*-axis with Ag(1)–N(1) and Ag(1)–N(2**) bond lengths of 2.265(8) and 2.255(6) Å, respectively, and a N(1)–Ag(1)–N(2**) angle of 161.3(3)°. These values are within the range generally observed for silver(I) coordination polymers of heterocyclic amines. The BF₄⁻ anion forms a strong Ag(1)–F(1*) bond of 2.633(9) Å, significantly shorter than the 2.714(5) Å found in the related 1-D [Ag(pyrazine)]BF₄ polymer.¹¹ Although BF₄⁻ is usually regarded as a non-coordinating anion, several instances of Ag–F bonds in BF₄⁻ salts have been reported,¹¹⁻¹³ some as short as 2.57(5) Å.¹⁴

Interestingly, the BF₄⁻ anions bridge silver centres on adjacent chains *via* longer Ag(1)–F(2), Ag(1)–F(3) and Ag(1*)–F(3) bonds of 2.841(9), 2.882(8) and 2.947(8) Å, respectively, to give rise to a two dimensional array (Fig. 3). The Ag–F interactions in **2** are considerably shorter than 3.2 Å, the sum of the van der Waals radii of silver and fluorine.¹⁵ The Ag(1)–F(4)

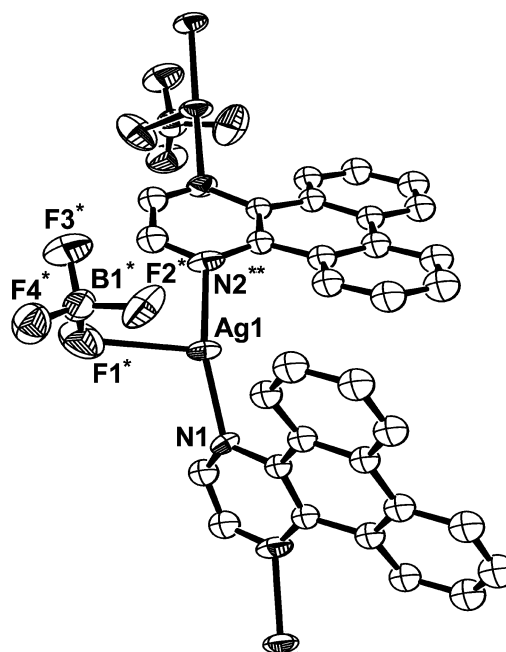


Fig. 2 One-dimensional chain structure of **2** (ORTEP, 33% ellipsoids). Hydrogen atoms removed for clarity. Selected bond lengths (Å) and angles (°): Ag(1)–N(1) 2.265(8), Ag(1)–N(2**) 2.255(6), Ag(1)–F(1*) 2.633(9), N(1)–Ag(1)–N(2**) 161.3(3). Symmetry operation * = $x-1, y, z$; ** = $-x+1/2, y+1/2, z$.

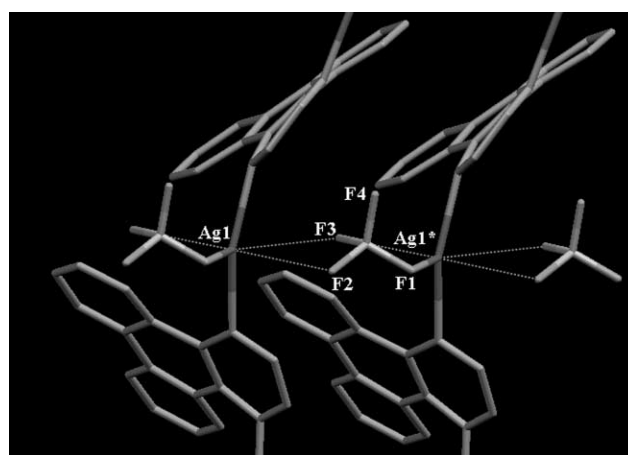


Fig. 3 Extended 2-D array of **2**. Hydrogen atoms removed for clarity. The Ag(1)–η²-BF₄⁻ interaction is shown as dotted lines. Ag(1)–F(2): 2.841(9) Å, Ag(1)–F(3): 2.882(8) Å, Ag(1*)–F(3): 2.947(8) Å.

distance is much longer, at greater than 3.9 Å. Thus, the BF₄⁻ anion acts as a bridging ligand, binding in an η²-fashion to adjacent Ag(I) centres. Only three of the four potential fluoroligands are utilized, and one of these also acts as a μ-fluoro bridge. This highly unsymmetrical η²-(F,F')-μ-(F')-η²-(F',F'')

bonding mode has not been previously observed for BF_4^- , although several examples of this anion acting as a symmetrically bridging $\eta^2\text{-}\mu\text{-}\eta^2$ ligand (utilizing all four fluoro-moieties) have been reported.^{13,16}

Another interesting feature of this crystal structure is the large deviation from planarity observed for the ligand (Fig. 3). In particular, the values of ϕ_1 and ϕ_2 are 12° and 14° , respectively. This represents an appreciable distortion from the conformation of the unbound ligand, which is expected to be approximately planar.¹⁷ It appears likely that this distortion arises in order to accommodate the steric demands introduced by the silver cations in close proximity to the bay hydrogens, H(1) and H(2). Similar distortions have been observed in triphenylene derivatives with bulky substituents at one or more of the bay positions.^{20–23} However, such examples have generally involved cases of groups linked covalently at these positions. The present system is, to the best of our knowledge, the first example of a significant disruption of the planar structure of a polycyclic aromatic hydrocarbon brought about by metal–ligand interactions.²⁴

In order to examine if this distortion is anion-dependent, the perchlorate analogue, $[\text{I}\cdot\text{AgClO}_4]$ (**3**), was synthesized† and structurally characterized.‡ The structures of **2** and **3** are very similar. A 13° distortion from planarity was found for the ligand in **3**, and the ClO_4^- anion exhibits an unsymmetrical $\eta^2\text{-}(O,O')\text{-}\mu\text{-}(O')\text{-}\eta^2\text{-}(O',O')$ bonding mode (previously unobserved) with Ag–O bond distances ranging from 2.765(14) to 2.951(16) Å.

The fact that the ligand, **1**, undergoes these distortions rather than using its π -system to coordinate the metal in an η^2 -fashion suggests that the energetic cost of twisting the aromatic ligand is rather modest. In order to confirm this hypothesis, we carried out semi-empirical and *ab initio* calculations on the ligand in both its unbound geometry and in the conformation observed for the coordination complex (*sans* metal). These calculations indicate that the energy required to twist the ligand is between 1.4 kcal mol⁻¹ (AM1) and 2.9 kcal mol⁻¹ (HF/3-21G*).²⁵ While the two methods disagree on the absolute magnitude of the distortion energy, both predict that it is insufficient to bias the ligand towards adopting an η^2 alkene-type coordination geometry.⁴

As can be seen in Fig. 3, the silver(I) centre lies appreciably (23°) out of the pyrazine ligand plane. This displacement undoubtedly also reduces the steric interactions between the bay hydrogens and the metal. If the silver(I) centre were situated in the plane of the ligand, as is usually observed,¹ even larger distortions of the ligand from planarity would be required to accommodate coordination.

The observation that heterocyclic amines with putatively hindered binding sites can readily distort in order to accommodate Ag(I) creates new avenues for constructing coordination polymers with novel architectures.

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Notes and references

† *Synthesis of 2*: A solution of AgBF_4 (0.017 g, 0.087 mmol) in ether (15 ml) was added dropwise in the dark to a stirred solution of **1** (0.020 g, 0.087 mmol) in ether (10 ml). A yellow precipitate of $[\text{I}\cdot\text{AgBF}_4]$ formed rapidly, was collected by filtration and dried under vacuum. Yield: 0.033 g (89%). Anal. Calcd. for $\text{C}_{16}\text{H}_{10}\text{N}_2\text{AgBF}_4$: C, 45.22; H, 2.37; N, 6.59. Found: C, 44.88; H, 2.33; N, 6.50. IR (KBr): 1607, 1482, 1434, 1385, 1267, 1061(νBF_4), 765, 723, 544, 521 cm⁻¹. *Synthesis of 3*: Using the same procedure as for **2**, a yellow precipitate of $[\text{I}\cdot\text{AgClO}_4]$ was obtained. Yield: 0.076 g (87%). Anal. Calcd. for $\text{C}_{16}\text{H}_{10}\text{N}_2\text{AgClO}_4$: C, 43.92; H, 2.30; N, 6.40. Found: C, 44.20; H, 2.41; N, 6.22. IR (KBr): 1606, 1484, 1438, 1390, 1340, 1268, 1194, 1182, 1114, 1067, 1026, 961, 916, 864, 816, 764, 726, 626, 616 cm⁻¹. Yellow crystals of **2** and **3** were

obtained *via* slow diffusion of diethyl ether solutions of the two reagents in an H-shaped tube at room temperature in the dark.

‡ *Crystal data*: $\text{C}_{16}\text{H}_{10}\text{N}_2\text{AgBF}_4$ (**2**); $M = 424.942$, orthorhombic, space group $Pbn2_1$, $a = 5.742(5)$, $b = 13.686(1)$, $c = 18.320(2)$ Å, $V = 1439.7$ Å³, $Z = 4$, $D_c = 1.960$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 14.29$ cm⁻¹, $T = 293$ K, 1784 data collected, 1510 unique, $R_1 = 0.042$, $wR = 0.050$ (observed data). $\text{C}_{16}\text{H}_{10}\text{N}_2\text{AgClO}_4$ (**3**); $M = 437.583$, monoclinic, space group Pn , $a = 10.668(2)$, $b = 5.5754(9)$, $c = 13.323(2)$ Å, $\beta = 111.963(15)^\circ$; $V = 734.9$ Å³, $Z = 2$, $D_c = 1.97$ g cm⁻³, $\mu(\text{Mo-K}\alpha) = 15.64$ cm⁻¹, $T = 293$ K, 1682 data collected, 1504 unique, $R_1 = 0.040$, $wR = 0.041$ (observed data). Data collection, structure solution and refinement of **2** and **3** were performed as described elsewhere.¹⁰ CCDC reference numbers 197738 and 209272. See <http://www.rsc.org/suppdata/dt/b3/b302264a/> for crystallographic data in .cif or other electronic format.

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