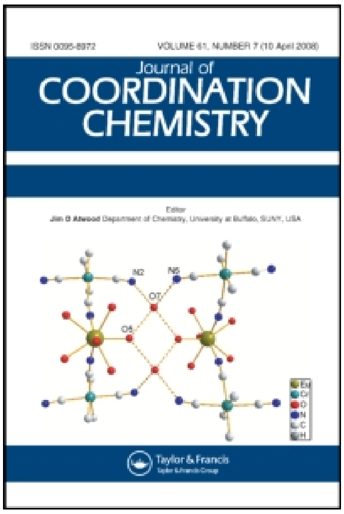

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Crystal structures of the coordination polymers formed between 1,2-bis(3'-pyridyl)ethyne and silver(I) trifluoromethanesulfonate

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Crystal structures of the coordination polymers formed between 1,2-bis(3′-pyridyl)ethyne and silver(I) trifluoromethanesulfonate

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The reaction of 1,2-bis(3′-pyridyl)ethyne with silver(I) trifluoromethanesulfonate yields two coordination networks. A one-dimensional double-stranded coordination polymer was formed in acetonitrile. The silver has a square-planar coordination geometry with weak coordination to one acetonitrile molecule and the triflate counter ion. The second network, formed in dichloromethane, is a complex three-dimensional network of interconnected one-dimensional zig-zag ribbons.

Keywords: Silver(I); Coordination polymer; 1,2-Bis(3′-pyridyl)ethyne

1. Introduction

The coordination chemistry of bipyridyl ligands has been extensively studied over the past decades. The most widely studied ligands are 4,4′-bipyridine and 2,2′-bipyridine [1]. These ligands (**1** and **2** in chart 1) have clear coordination preferences that are determined by the position of the nitrogen atoms in each ligand. Thus 2,2′-bipyridine has the nitrogen atoms positioned to complex a metal cation in a *cis* manner. In contrast 4,4′-bipyridine has the nitrogen atoms at opposite ends of the molecule and is well positioned to form one-dimensional coordination polymers. Indeed the use of polypyridyl ligands in the fields of crystal engineering and supramolecular chemistry is now well established [2]. We embarked on a study of less common pyridine-based ligands several years ago [3]. A ligand that we made and investigated is 1,2-bis(3′-pyridyl)ethyne [4]. This ligand has the nitrogen atoms positioned such that simple coordination complexes cannot be formed and any coordination polymer cannot be a simple linear ribbon.

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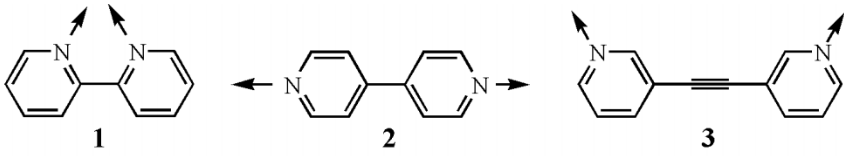


Chart 1

We initially characterized two complexes with copper(I) bromide [4a]. The complexes showed two different conformations of the ligand. In one conformation the ligand was essentially coplanar with the nitrogen atoms oriented in opposite directions as shown in chart 2, conformation **A**. The second high-energy, slightly bent, conformation had the two pyridyl rings almost orthogonal as shown in chart 2, conformation **B**. In the coordination network formed between **3** and copper(I) iodide the ligand also adopted the *trans* conformation **A** [4b].

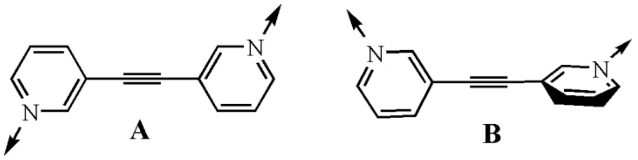


Chart 2

In this article we describe two silver(I) coordination networks formed with the dipyridyl ligand **3**.

2. Experimental

2.1. *Synthesis*

All chemicals and solvents were purchased from Aldrich and used as received. The preparation of **3** has been reported [4a].

2.1.1. Reaction of 3 with silver(I) trifluoromethanesulfonate in acetonitrile. A slurry of silver trifluoromethanesulfonate (25.6 mg, 0.1 mmol) and 1,2-bis(3′-pyridyl)ethyne (18.1 mg, 0.1 mmol) in acetonitrile (3 cm^3) in a screw-cap vial was sealed and heated gently until a homogeneous solution was obtained. The vial was placed in the dark and crystals started to form after 24 h. The crystals, **4**, were block-shaped. Anal. Calcd. for $C_{17}H_{17}Ag\ F_3N_4O_3S$ (%): C, 39.32; H, 2.72; N, 10.79. Found: C, 39.75; H, 2.84; N, 11.19.

2.1.2. Reaction of 3 with silver(I) trifluoromethanesulfonate in the presence of 1,3-dicyanobenzene. A slurry of silver trifluoromethanesulfonate (25.6 mg, 0.1 mmol), 1,2-bis(3′-pyridyl)ethyne (18.1 mg, 0.1 mmol) and 1,3-dicyanobenzene (12.8 mg, 0.1 mmol) in dichloromethane (10 cm^3) in a screw-cap vial was sealed and heated gently until a homogeneous solution was obtained. The vial was placed in the dark

Table 1. Crystal data and structure refinement for **4** and **5**.

Compound	**4**	**5**
CCDC identification code	251932	251933
Chemical formula	$C_{34}H_{28}Ag_2F_6N_8O_6S_2$	$C_{52}H_{32}Ag_4F_{12}N_8O_{12}S_4$
Formula weight	1038.50	1748.58
Crystal system, space group	Triclinic, $P\bar{1}$	Orthorhombic, $C222_1$
Unit cell dimensions, a (Å)	7.1526(3)	10.3483(5)
b (Å)	11.1318(5)	12.5746(6)
c (Å)	13.4809(6)	45.802(2)
α (°)	76.0200(10)	90
β (°)	82.6110(10)	90
γ (°)	78.5390(10)	90
Volume, $Å^3$	1017.13(8)	5960.0(5)
Temperature, K	173(2)	173(2)
Z, Calculated density, $Mg\,m^{-3}$	1, 1.695	4, 1.949
Absorption coefficient, mm^{-1}	1.146	1.540
Reflections collected/unique	7183/4347 [R(int) = 0.0159]	18803/6600 [R(int) = 0.0445]
Final R indices [$I > \sigma(I)$]	$R1 = 0.0267$, $wR2 = 0.0704$	$R1 = 0.0768$, $wR2 = 0.206$

and crystals started to form after 24 h. The crystals, **5**, had the shape of thin plates. Anal. Calcd. for $C_{13}H_8Ag\ F_3N_2O_3S$ (%): C, 35.72; H, 1.84; N, 6.41. Found: C, 35.46; H, 1.73; N, 6.62.

2.2. *X-Ray data collection, structure solution, and refinement*

A colorless block of coordination complex **4** with dimensions 0.35 × 0.35 × 0.25 mm and a colorless plate of complex **5** of dimensions 0.25 × 0.20 × 0.05 mm were selected for X-ray analysis. The X-ray data for **4** and **5** were collected on a Siemens CCD area detector-equipped diffractometer with Mo-Kα radiation. The structures were solved using SHELXS-97 and refined with SHELXL-97 [5]. Hydrogen atoms were included in the calculated positions. The crystallographic data are collected in table 1. Ortep 3 was used to prepare the figures [6].

3. Results

Elemental analysis of complex **4** formed on reaction of ligand **3** and silver(I) trifluoromethansulfonate in acetonitrile solution indicated that a 1 : 1 complex was formed with 2 molecules of included acetonitrile solvent. The crystal structure revealed a double-strand one-dimensional coordination polymer. There is one ligand, one silver(I) trifluoromethanesulfonate anion and two acetonitrile molecules in the asymmetric unit as shown in figure 1.

The ligand adopts the essentially planar *trans* conformation **A** shown in chart 2 to form a wave-like, linear, double-strand coordination polymer as shown in figure 2.

The nitrogen–silver–nitrogen bond is essentially linear with a N(1)–Ag(1)–N(2) angle of 172.89(6)° and normal silver–nitrogen bond distances Ag(1)–N(1) and Ag(1)–N(2) of 2.1895(17) and 2.1963(17) Å, respectively. The coordination sphere about each silver is completed with a linear but weak interaction to the counter ion and an acetonitrile molecule with an oxygen–silver–nitrogen bond angle, O(2)–Ag(1)–N(3), of 177.12°. The silver–oxygen bond distance, Ag(1)–O(2), of 2.837 Å is significantly longer than other silver–triflate bond distances which are reported to be as short as 2.509 Å [7].

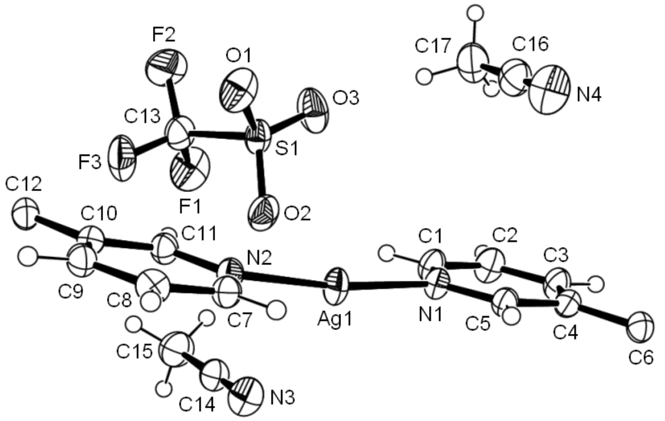


Figure 1. Ortep plot of the asymmetric unit in complex **4** formed between 1,2-bis(3′-pyridyl)ethyne and silver(I) trifluoromethanesulfonate in acetonitrile. Thermal ellipsoids are drawn at 50% probability.

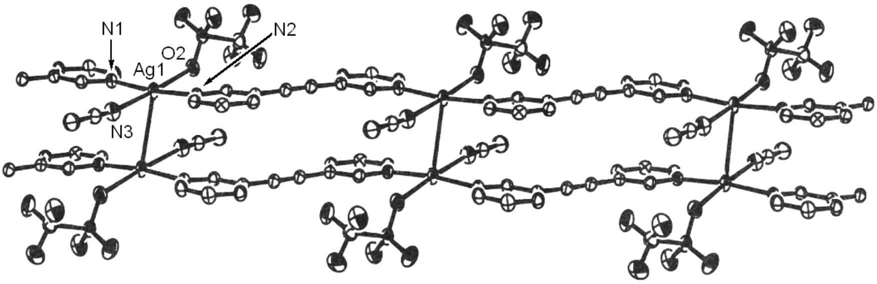


Figure 2. Perspective view of the double-strand linear coordination polymer, **4**, formed between 1,2-bis(3′-pyridyl)ethyne and silver(I) trifluoromethanesulfonate in acetonitrile.

The acetonitrile silver–nitrogen bond distance, Ag(1)–N(3), of 2.793 Å is also much longer than the distance in the tetrakis acetonitrile silver(I) salts where bond distances ranging from 2.18 to 2.29 Å have been reported [8]. The oxygen–silver–pyridine nitrogen bond angle O(2)–Ag(1)–N(1) is 88.12° while the acetonitrile–silver–pyridine bond angle N(3)–Ag(1)–N(1) is 90.80°. There is a close silver–silver contact of 3.3001 Å which is longer than the silver–silver distance in metallic silver of 2.88 Å [9] but shorter than the sum of the van der Waals radii of two silver atoms 3.44 Å [10]. The coordination geometry about silver is square pyramidal with a dominant linear pyridine–silver–pyridine interaction. The double-strand ribbon-like structure has close contact between the organic ligands with a centroid–centroid distance of approximately 3.66 Å and a closest contact of approximately 3.55 Å.

The second structure, complex **5**, is a more complex interwoven three-dimensional structure in which the asymmetric unit contains two bipyridyl ligands **3**, three unique silver cations, and two unique trifluoromethanesulfonate anions as shown in figure 3.

The pyridyl–silver interaction is linear with the ligand in the *trans* conformation and interconnected one-dimensional ‘zig-zag’ ribbons are formed. A single strand is shown in figure 4. The silver–nitrogen bond lengths are normal with distances

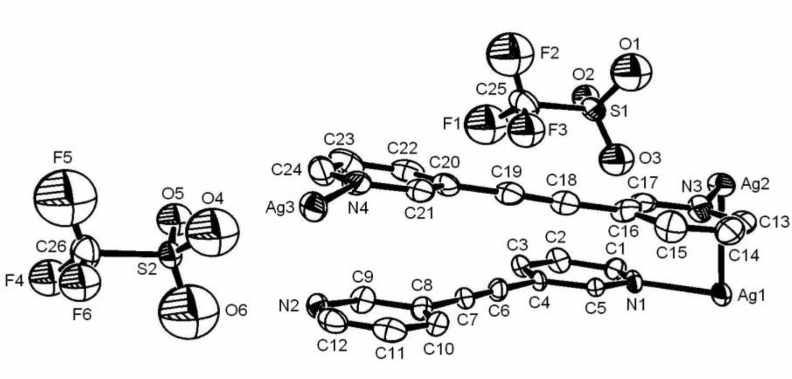


Figure 3. Ortep plot of the asymmetric unit in complex **5** formed between 1,2-bis(3′-pyridyl)ethyne and silver(I) trifluoromethanesulfonate with thermal ellipsoids drawn at 50% probability.

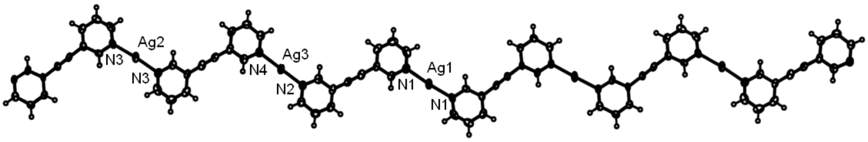


Figure 4. View of a single strand of the coordination network, **5**, formed between dipyridyl ligand **3** and silver(I) trifluoromethanesulfonate in dichloromethane solvent.

Ag(1)–N(1), Ag(2)–N(3), Ag(3)–N(2) and Ag(3)–N(4) of 2.146(8), 2.157(10), 2.169(9) and 2.189(9) Å, respectively. The coordination geometry is essentially linear for each of the three unique silver atoms with nitrogen–silver–nitrogen bond angles of 168.6(5), 176.2(6) and 173.0(4)° for N(1)–Ag(1)–N(1#1), N(3)–Ag(2)–N(3#1) and N(2)–Ag(3)–N(4), respectively.

The zig-zag strands pack together to form two-dimensional undulating sheets. Adjacent two-dimensional sheets have the individual strands running at an oblique angle to each other as shown in figure 5 where two strands from each of two adjacent layers are shown. Thus the two strands labeled X on the left of figure 5 cross over the two strands labeled Y on the left of the figure so that the positions of the two pairs of strands is reversed on the right side of the figure. Each strand has a series of weak silver–silver interactions with the layers above and below it as shown in figure 5. There are multiple π–π stacking interactions between adjacent pyridyl rings as indicated in figure 5. The centroid–centroid distance is 3.548 Å between pyridyl rings C(8)–N(2) and C(24)–N(4) and 3.612 Å between pyridyl rings C(5)–N(1) and C(17)–N(3).

4. Discussion

The original idea behind this research involved complexation of silver cations by a strong donor dipyridyl ligand along with a weaker dinitrile ligand [11]. We had reasoned that the cooperativity between the two ligands might promote the formation of hexagonal structures as shown in scheme 1.

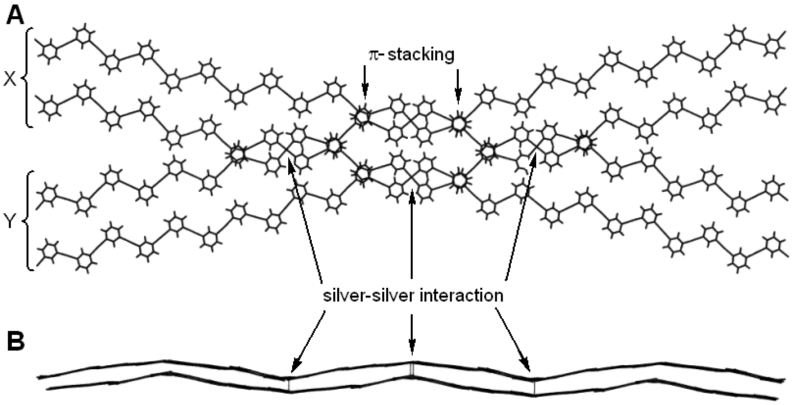
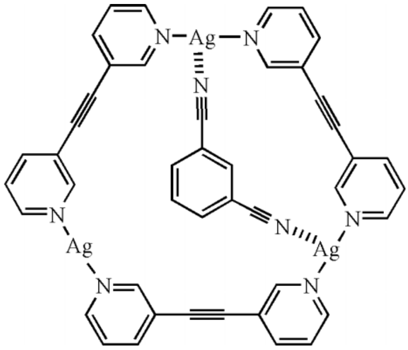


Figure 5. View showing the three-dimensional network **5** formed between dipyridyl **3** and silver(I) trifluoromethanesulfonate showing the pyridine–silver and silver–silver connectivity. The trifluoromethanesulfonate anions omitted for clarity.



Scheme 1.

We first mixed the dipyridyl ligand **3** with silver(I) trifluoromethanesulfonate in acetonitrile and collected the crystals, **4**, formed for X-ray crystallographic analysis. The crystal structure showed the incorporation of the acetonitrile with the nitrile–silver bond distance significantly longer that the silver–pyridine bond distance as expected. We were however disappointed that the 1,3-dicyanobenzene was not incorporated in the crystalline material, **5**, formed in its presence. Both structures are dominated by a strong linear coordination of the dipyridyl ligand. In the systematic study of silver(I) coordination complexes Moore et al. reported that the linear geometry was most common [12]. Our future work in this area will focus on the use of 1,3,5-tricyanobenzene to orient and form hexagonal coordination complexes.

Supplementary material

CCDC 251932 and CCDC 251933 contain the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge

Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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