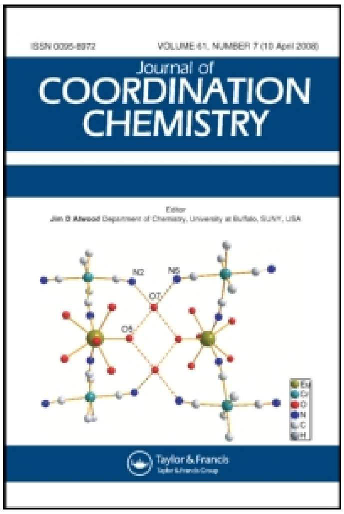

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Competition between coordination bonds and hydrogen bonds: the nitrile-silver(I) interaction using dicyanobithiophene as ligand

Wendy A. Sears[a]; Marissa L. Hudolin[a]; Hilary A. Jenkins[b]; Robert C. Mawhinney[a]; Craig D. Mackinnon[a]
[a] Department of Chemistry, Lakehead University, Ontario, Canada [b] Department of Chemistry, Saint Mary's University, Canada

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Competition between coordination bonds and hydrogen bonds: the nitrile-silver(I) interaction using dicyanobithiophene as ligand

WENDY A. SEARS†, MARISSA L. HUDOLIN†, HILARY A. JENKINS‡,
ROBERT C. MAWHINNEY† and CRAIG D. MACKINNON*†

†Department of Chemistry, Lakehead University,
955 Oliver Rd., Thunder Bay, Ontario, P7B 5E1, Canada
‡Department of Chemistry, Saint Mary's University,
Halifax, Nova Scotia, B3H 3C3, Canada

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Reactions of the ligand 5,5′-dicyano-2,2′-bithiophene (T_2CN_2) with a variety of silver(I) salts are presented. In most cases, the ligand precipitates by itself without incorporating the silver(I) metal. However, when the counterion is triflate, in benzene or THF, a coordination compound is formed. The crystal structure of the species grown from benzene, a double-stranded one-dimensional polymer, is reported. In this structure, the bithiophene ligand is twisted into the uncommon *syn* orientation. The reasons for the lack of reactivity of the ligand are discussed by comparing the relative strengths of the interligand hydrogen bond with the ligand–metal bond.

Keywords: Silver(I) complexes; Oligothiophenes; Self-assembly; Hydrogen bonds; Nitrile

1. Introduction

In the node and spacer method of crystal engineering, the bonding geometry of the metal node determines the crystalline geometry while the dimensions are controlled by the size of the ligand spacer [1]. In the case of d^{10} metal cations, however, there is no geometric preference because there is no ligand-field stabilisation energy to control the orientation of the ligands. The silver(I) cation is typical of these d^{10} metals, in that the crystal structure is likely to be determined by more subtle effects such as ligand : metal ratio [2], solvent [3–5], or the nature of the counterion [6–11], rather than by any metal-directed templating. Silver(I) is also of interest because it forms coordination bonds with many ligand moieties, including pyridyls [9, 12–15], acetylides [16], phosphines [17–22], sulfonates [23, 24], and nitriles [21, 25–28].

We have chosen to use the aromatic nitrile 5,5′-dicyano-2,2′-bithiophene (T_2CN_2) as our ligand. Oligomers of thiophene are well-known organic semiconductors [29, 30] and have a π-conjugated aromatic core, which opens the possibility of cation–cation

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*Corresponding author. Email: craig.mackinnon@lakeheadu.ca

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communication for use in molecular electronics [31, 32]. The sulfur heteroatom may interact with the silver(I) in a soft acid-base interaction [33] creating cross-links, as it does with pyridine [34, 35], or it may remain uncoordinated [36–38] and available for further reaction. If the heteroatom remains uncoordinated, and if it has an affinity for an environmental species of interest, the resultant coordination compound may function as a chemical sensor [39]. The low donor ability of the thiophene sulfur is not a problem as it may, in fact, assist in reversibility of the chemical sensing reaction. The coordinative flexibility of silver(I) may also allow exchange with an environmental species.

In this article, we present the results of our investigations into the reaction of silver(I) salts (counterions: triflate, nitrate, hexafluorophosphate, and hexafluoroantimonate) with T_2CN_2. In many cases, no reaction occurs, and we propose that the interligand hydrogen bonds are comparable in strength with the nitrile–Ag(I) interaction, leading to crystallization of ligand instead of formation of coordination bonds. In two cases, however, the right conditions are found to favour formation of coordination complexes. The crystal structure of one of these is presented, showing a 1-D coordination polymer linked by nitrile–Ag(I) interactions, in which the bithiophene core is oriented in the uncommon *syn* orientation.

2. Results and discussion

2.1. *Synthesis and characterisation*

In a typical experiment, a mixture of T_2CN_2 and a silver(I) salt were combined in 15–20 mL of a dried and degassed organic solvent. The mixture was sealed in a Pyrex tube and heated to 100°C until the ligand dissolved (T_2CN_2 has negligible solubility at room temperature). The tube was then placed in a tube furnace and the temperature lowered from 100°C to room temperature at a rate of 1° per h. As shown in table 1, four silver salts and six solvents were tested, with 1 : 1 molar ratios of Ag(I): T_2CN_2. In a few cases, 3 : 2 ratios were also attempted, but the results were identical to those using a 1 : 1 ratio. Concentrations of reactants were optimised to produce crystalline compounds, unless decomposition occurred (resulting in a black powder, characterized as

Table 1. Isolated Products[a] of the reaction of AgX with T_2CN_2 (1 : 1 molar ratio).

	Anion (X-) in AgX salt			
Solvent	NO_3^-	$CF_3SO_3^-$	PF_6^-	SbF_6^-
CH_3CN	NR	NR[b]	NR[b]	NR[b]
C_6H_6	NR	1 : 1[b]	NR[b]	–[c]
C_7H_8	NR	NR	NR	NR
THF	Decomp	1 : 1	Decomp	Decomp
C_2H_5OH	NR	NR	Decomp	Decomp
CH_3OH	–	Decomp	Decomp	–

[a] "NR" (no reaction) means the isolated product is unreacted ligand; "decomp" means the reaction mixture decomposed.

[b] The same result was obtained when a 3 : 2 molar ration was used.

[c] Insolubility of the silver salt prevents reaction in this solvent.

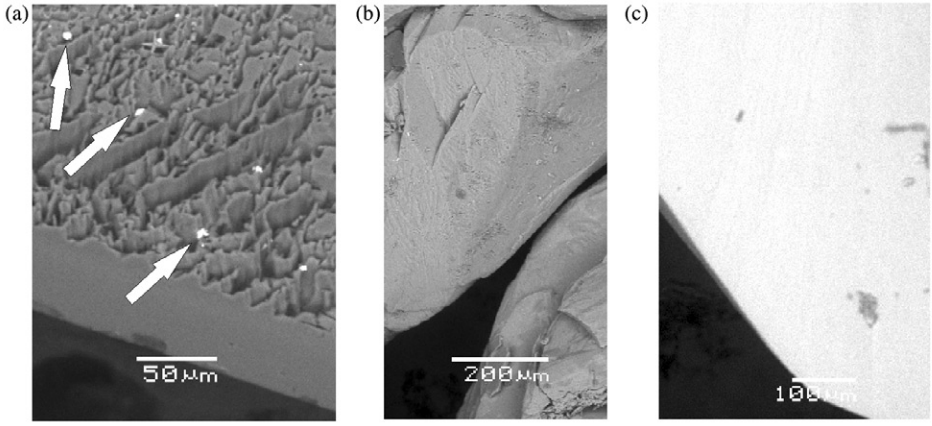
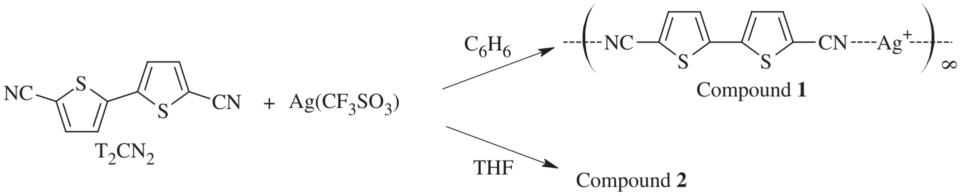


Figure 1. Energy dispersive spectroscopy (EDS) results for the reaction of T_2CN_2 with AgCF3SO3 (1 : 1 molar ratio). In these pictures, shading is graded from low (dark) to high (light) molar mass. (a) Acetonitrile solvent; arrows point to bright spots indicating trapped AgCF3SO3. (b) Benzene solvent (Compound 1). (c) THF solvent (Compound **2**).



Scheme 1. Synthesis of the coordination polymers **1** and **2**.

silver oxides). The solids were analyzed by mass spectrometry, infrared spectroscopy, and semiquantitative energy dispersive spectrometry (EDS), figure 1. In the majority of cases, no reaction occurred, and the isolated crystalline product was T_2CN_2. Often, EDS revealed pockets of silver salt trapped within the ligand lattice, as shown in figure 1(a). The nitrile stretching frequency in the IR was identical to that of pure ligand ($2195\,cm^{-1}$).

In two cases, however, coordination compounds with a 1 : 1 ratio of silver to ligand were isolated, scheme 1. Both contained triflate as the anion. One was isolated from benzene (compound **1**) and the other from THF (compound **2**). There is a small but obvious shift in the nitrile stretch (from 2195 to $2205\,cm^{-1}$), and the uncorrected EDS spectrum (figures 1b and c) gave sulfur : silver ratios of 2.48 : 1. There are three sulfur atoms in the compounds (two in T_2CN_2 and one in the triflate), but the different chemical environments of the two sulfurs make it difficult to calibrate the EDS instrument to a higher degree of accuracy. The chemical formula of **1** was confirmed by single-crystal X-ray diffraction and combustion analysis to be $T_2CN_2AgOTfC_6H_6$, which includes one molecule of benzene solvent per formula unit.

Upon exposure to air, the clear, colourless silver(I) complexes **1** and **2** become opaque. The nitrile IR stretch remains identical to that of the pristine complex, indicating that the nitrile-silver(I) interaction is unaffected. We conclude the instability is due to loss of the solvent of crystallization and/or reaction with atmospheric water at the silver cation. Combustion analyses of exposed samples show an increase in the H : C ratio, consistent with this hypothesis. The process is irreversible. When sealed under N_2, the complexes are indefinitely stable (months), with no photodegredation even if left under ambient lighting on the laboratory bench.

2.2. *Crystal structure of complex 1*

We have obtained the X-ray crystallographic structure of **1**. The details of the refinement are given in table 2 and selected bond lengths and angles in table 3. As shown in figure 2, the compound is a one-dimensional coordination polymer held together by nitrile–silver(I) bonds without bonding to the thiophene sulfurs, in spite of the potential for a soft acid-soft base interaction. Figure 3 shows the local cation environment, which is five-coordinate distorted trigonal bipyramidal with three short equatorial bonds and two longer axial contacts. Presumably the significant deviation from 120° bond angles in the trigonal plane (see table 3) is not energetically detrimental due to the lack of a crystal-field geometric preference for Ag^+. The trigonal plane contains two Ag^+–N (nitrile) bonds (of the 1-D chain) and one Ag^+–O (triflate) bond [8, 40, 41]. The average $C\equiv N–Ag^+$ distance of 2.167 Å is similar to, if slightly longer than, other aromatic nitrile–silver(I) compounds; e.g. when the ligand is

Table 2. Crystallographic data and structural refinement for compound **1** ($T_2CN_2 \cdot AgCF_3SO_3 \cdot C_6H_6$).

CCDC identification code	286509
Chemical formula	$C_{17}H_{10}AgF_3N_2O_3S_3$
Formula weight	551.32
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.5152(7)
b	10.4989(8)
c	10.5505(8)
α	69.338(1)
β	87.358(1)
γ	85.375(1)
Volume (Å^3)	982.8(1)
Temperature (K)	223(2)
Z, density ($Mg\,m^{-3}$)	2, 1.863
Linear absorption coefficient μ(Mo-Kα, mm^{-1})	1.394
Reflections collected/unique reflections	7313/3464
Goodness of fit	1.089
Largest peak, hole in final difference-Fourier map	0.899, −1.267
Final R value (all data)	$R_1 = 0.0431$, $wR_2 = 0.0856$

Table 3. Selected bond length and angles for compound **1** ($T_2CN_2 \cdot AgCF_3SO_3 \cdot C_6H_6$).

Ag–N(1)	2.173(3)	N(1)–Ag–N(2)	157.2(1)
Ag–N(2)	2.160(3)	N(1)–Ag–O(1)	94.0(1)
Ag–O(1)	2.461(3)	N(2)–Ag–O(1)	103.8(1)
N(1)–C(1)	1.143(4)	C(2)–C(1)–N(1)	177.9(3)
N(2)–C(10)	1.139(4)	C(9)–C(10)–N(2)	177.7(4)
C(2)–C(3)	1.3619(4)	C(1)–N(1)–Ag	162.2(3)
C(3)–C(4)	1.404(4)	C(10)–N(2)–Ag	162.8(3)
C(4)–C(5)	1.366(4)		

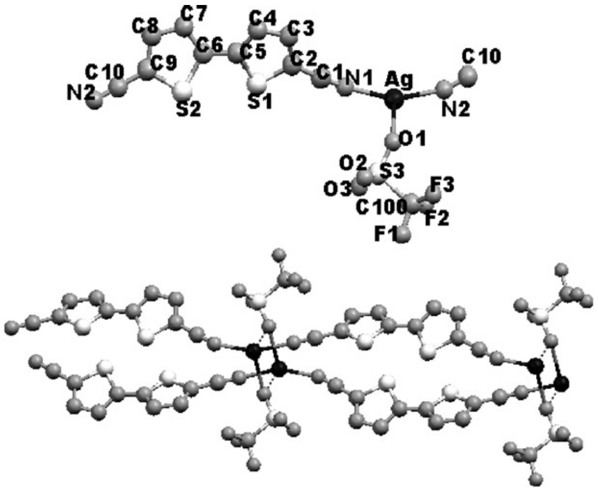


Figure 2. Top: repeat unit of the compound **1** and atomic labelling scheme. Bottom: Representation of the double-strand structure of the coordination polymer 1. The two strands are linked by bridging oxygens on the triflate anion. C, N, O, and F are grey; S is white; Ag is black. Hydrogen atoms are omitted for clarity.

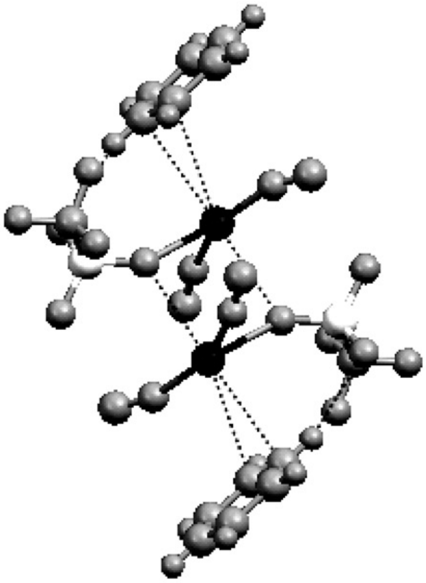


Figure 3. Local bonding environment of the silver cations in compound **1**. Shading is the same as in figure 2.

dicyanobiphenyl the average distance is 2.136 Å [2], while for the bipyridyl equivalent it is 2.156 Å [35]. The Ag^+–O (triflate) distance (2.461 Å) is short enough to be considered a silver(I)–oxygen bond. While this length is considerably shorter than the equivalent anion-silver(I) interaction in the complexes containing biphenyl (2.60 Å) [2] and bipyridyl (2.689 Å) [35] dinitrile ligands, it is not the shortest known (e.g., one pyrazine-containing compound has a Ag^+–O(triflate) bond of 2.325 Å [40]).

The strength of the bond to the triflate does have a noticable effect on the C ≡ N–Ag$^+$ bond angle. The nitrile lone pair is putatively at a 180° angle to the C≡N bond; in **1**, the angle is reduced to 163° as the oxygen "pulls" the silver cation towards itself in the trigonal plane [42].

Interestingly, the triflate anions are all on the same side of the 1-D coordination polymer chain. This does not lead to a polar structure, however, as two polymer strands are linked through a bridging Ag$^+$–O(triflate)–Ag$^+$ interaction, shown in figure 3 [43–46]. This interaction takes up one of the axial Ag$^+$coordination sites, while the other is taken up by a molecule of benzene, coordinated in an η^2-fashion [40, 44, 45, 47]. The Ag(I)–Ag(I) distance is 3.78 Å, which is a weak interaction at best. The double strand is linked to its neighbours by hydrogen bonds between the ligand ß-hydrogens and the oxygens and fluorines on the triflate.

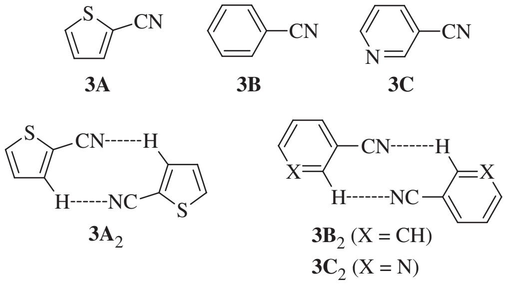
Oligothiophenes generally crystallize with their rings in mutually *anti* arrangements, which gives nearly flat oligomers (with dihedral angles between rings of no more than a few degrees) in order to maximise inter-ring conjugation [48–52]. The *anti* configuration of T_2CN_2 would give an off-axis, rod-type ligand. Such ligands normally form a wavy, sinusoidal polymer [12], which could allow either a 180° or a non-180° bond angle at the silver ion. Instead, in this complex, the bithiophene core is twisted into the less energetically favourable *syn* orientation, giving the wide nitrile–Ag–nitrile bond angle (157°) [42]. The dihedral angle between the thiophene planes is 26°.

2.3. *Discussion and computational results*

Changes in counterion size and/or donor ability can have significant effects on the crystal structure of a coordination compound. In our case, it appears that the effect is so severe that it governs whether or not a reaction takes place. The donor ability of the counterion must be a strong enough to satisfy the metal coordination sphere, but not so strong as to displace the metal-nitrile interaction. Because donor ability of our four anions are in the order $NO_3^- > CF_3SO_3 > PF_6^- \approx SbF_6$ [53, 54], only triflate achieves the delicate balance necessary to allow a coordination complex to form.

The identity of the solvent can also have a significant controlling effect on the type of structure formed. In acetonitrile, for example, we see no reaction. We are not surprised as alkyl nitriles can be used as ligands for silver(I) [26, 55–57]. The overwhelming number of acetonitrile molecules interfere with the coordination sites on the silver. In addition, and perhaps more importantly, hydrogen bonding will occur between the ligands and the solvent, and this interaction is likely stronger than that between the ligand and the metal cation. Synthesis of silver complexes is also common in alcohols [2, 23, 35, 54, 55], but they are almost always performed at room temperature. In our case, the elevated temperature leads to decomposition. It is unclear at this time why a compound is formed in benzene but not in toluene.

We attribute the general lack of reactivity between the nitrile and the cation to the strength of the interligand hydrogen bond. Although the crystal structure of T_2CN_2 is unknown (and despite repeated attempts on our part to grow crystals), the structures of T_nCN_2 ($n = 3$ to 5) are known and show a pairwise $\cdots$ H hydrogen bond, $3A_2$, for a total of 4 H-bonds per unit (two on each end) [51]. Thus, the combination of four interligand CN $\cdots$ H hydrogen bonds must be stronger than two CN $\cdots$ Ag(I)



Scheme 2. Compounds investigated by computational modelling.

Table 4. Selected computational results on the optimized structures of three aromatic nitriles.

Compound	Q on nitrile N	Q on α-H	ρ on nitrile N	Stabilization of dimer (kcal mol^{-1})
3A	−1.108	0.119	0.557	4.78
3B	−1.129	0.101	0.557	4.15
3C	−1.115	0.110[a] 0.113[b]	0.559	4.15

[a] 2-position.
[b] 4-position.

interactions, leading to crystallization of ligand instead of formation of a coordination compound. A similar pairwise interaction is present in dicyanobenzene [58, 59], however, and it readily forms coordination compounds with silver(I) [2, 25, 28, 60, 61]. Thus, we performed DFT calculations to try and understand the details of why T_2CN_2 does not coordinate as readily as phenyl nitriles.

We modelled three monomers, 3A, 3B, and 3C shown in scheme 2. The results are given in table 4 as the calculated charges (Q) on the nitrile N and on the hydrogen α to the nitrile, as well as the charge densities (ρ) on the nitrile N. 3-cyanopyridine 3C was chosen because it is the isomer present in the nitrile–silver(I) compounds $(C_5H_3N)_2(CN)_2AgX$ ($X = NO_3$, CF_3SO_3) [35]. As shown in table 4, the $\delta+$ on the H-atom is largest for thiophene, while the $\delta-$ on the nitrile nitrogen is the smallest. It is tempting to conclude that the thiophene nitrile has the lowest electron density to donate to the silver(I) cation, so it forms the weakest interaction with silver(I). Meanwhile, the $CN \cdots H$ interaction is comparable to those of benzene and pyridine because of the increased $\delta+$ on the H-atom. We also calculated the gas-phase energies of three dimers containing pairwise hydrogen bonds ($3A_2$, $3B_2$, and $3C_2$), and it appears that the thiophene dimer $3A_2$ is the strongest, although the difference might reflect the inclusion of a third-row sulfur in the calculation, rather than any real difference in bond strength. Even if the relative numbers are accurate, the difference might be small enough to become negligible in solution. However, the trend does seem to confirm our hypothesis that the thiophene nitrile has the weakest donating ability, while the interligand hydrogen bond is similar to that of benzene and pyridine nitriles. Therefore, thiophene nitriles are more likely to crystallizes by themselves instead of forming ligand-Ag^+ bonds.

3. Conclusion

Oligothiophene dinitriles have a lower ability to form complexes with silver(I) salts than do dinitriles of benzene and pyridine. The lower donating ability of the nitrile and the comparable strength of interligand hydrogen bonds generally causes the T_2CN_2 ligand to crystallise from solution without incorporation of the metal centre. However, under the right combination of anion and solvent, an unusual 1-D polymer is formed, containing T_2CN_2 in the uncommon *syn* orientation.

4. Experimental section

4.1. *Materials and characterisation*

The known ligand T_2CN_2 [62] was prepared by the literature method [63] of reacting copper(I) cyanide with dibromobithiophene (T_2Br_2) [64] in refluxing quinoline; it was purified by sublimation in a pot sublimer. Silver salts were purchased from Aldrich and used as received. Solvents (Anachemia) were HPLC grade and dried by distillation under N_2 from sodium (toluene), sodium/benzophenone (THF, benzene), magnesium (alcohols), or P_2O_5 (acetonitrile). IR spectra were recorded on a Perkin-Elmer model 1320 infrared spectrometer. Elemental analyses were performed on a CEC (SCP) 240-XA analyzer. EDS were recorded on a JEOL JSM-5900LV Variable Pressure SEM with a built-in Link ISIS EDS with a Super ATW Light Element Detector; ratios are uncalibrated ($\pm 20\%$). Crystals were grown in an Applied Test Systems model 3210 split tube furnace attached to a series 2404 3-zone temperature control system. Computational results were obtained with Gaussian98 [65], using the PBE0 hybrid density functional and the 6-311++G(2df pd) basis set (to minimize any basis set superposition error). The charges (Q) and charge densities (ρ) were obtained using Bader's Atoms-in-Molecules theory as implemented in the AIMPAC package. Computational facilities were supplied by the Centre for Research in Molecular Modelling (Concordia University).

4.2. *Synthesis*

4.2.1. General synthetic procedure. The ligand T_2CN_2 (20 mg, 0.093 mmol) and an equimolar amount of $AgNO_3$ (15 mg), $AgCF_3SO_3$ (23 mg), $AgPF_6$ (23 mg), or $AgSbF_6$ (31 mg) were added to a sealable glass tube (approx. dimensions 20 mm diameter × 150 mm). Dried solvent (15–20 mL of toluene, benzene, THF, or acetonitrile) was added and the mixture subjected to one freeze-pump-thaw cycle to remove most of the dissolved N_2 gas. The mixture was heated to 100°C for at least two hours (until the solids dissolved). Crystal growth was effected by cooling from 100 to 25°C at a rate of $1^\circ\,h^{-1}$. Either a black decomposition product or long, yellow, needle-like crystals were isolated in every case except the two discussed below. The yellow crystals, characterized by semiquantitative EDS, contained only organic species (including sulfur). Only small pockets of silver-containing species were imbedded in the organic phase. IR spectra were identical to that of the unreacted ligand.

4.2.2. Synthesis of $T_2CN_2 \cdot AgCF_3SO_3 \cdot C_6H_6$ (1). T_2CN_2 (20 mg, 0.093 mmol) and $AgCF_3SO_3$ (23 mg, 0.093 mmol) were added to a sealable glass tube. Dry benzene (14 mL) was added and the mixture subjected to one freeze-pump-thaw cycle. The tube was flame-sealed and heated to 100°C, at which temperature all the solids dissolved. The solution was then cooled to 25°C at a rate of $1^\circ\ h^{-1}$. Flat, elongated hexagons of colorless crystals were formed. IR (nujol mull): 3083 (w), 2205 (s), 1417 (m), 1275 (s), 1222 (s), 1174 (s), 1050 (m), 1018 (s), 872 (m), 798 (s). EDS: ratio of S : Ag Calcd 3.00; found 2.47. Anal. Calcd for $C_{17}H_{10}AgF_3N_2O_3S_3$ (%): C, 37.03; H, 1.83; N, 5.08. Found C, 36.69; H, 2.02; N, 4.90.

4.2.3. Synthesis of $T_2CN_2 \cdot AgCF_3SO_3 \cdot$ THF (2). T_2CN_2 (20 mg, 0.093 mmol) and $AgCF_3SO_3$ (23 mg, 0.093 mmol) were added to a sealable glass tube. Dry THF (20 mL) was added and the mixture subjected to one freeze-pump-thaw cycle. The tube was flame-sealed and heated to 100°C, at which temperature all the solids dissolved. The solution was then cooled to 25°C at a rate of $1^\circ\ h^{-1}$. Colourless rhomboid blocks of very small dimensions were isolated. IR (nujol mull): 3063 (w), 2205 (s), 1258 (s), 1205 (s), 1153 (s), 1003 (s), and 798 (m). EDS: ratio of S : Ag calculated 3.00; found 2.48.

4.3. *Crystallography*

4.3.1. Crystallographic study of $T_2CN_2 \cdot AgOTf \cdot C_6H_6$. Unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using DENZO reflection data, systematic absences were consistent with the triclinic space group $P\bar{1}$. The SHELXTL-NT V6.1 (Sheldrick, G.M.) suite of programs was used to solve the structure by direct methods. Subsequent difference Fourier synthesis allowed the remaining atoms to be located. The hydrogen atoms were calculated geometrically and were included as riding on their respective carbon atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. CCDC-286509 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif

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