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FULL PAPER

Coordination polymer complexes of 4,4′-dipyridyldisulfide and AgX (X = PF_6^-, ClO_4^-, OTs^-, NO_3^-, BF_4^-) with twisted rhomboid networks, 2-D sheets, and 1-D chain structures

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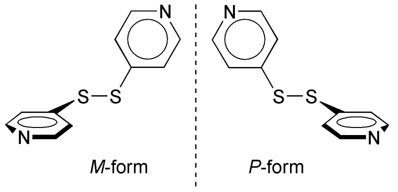
Several Ag^I coordination polymers linked by the –S–S– bridged ligand 4-PDS (= 4,4′-dipyridyldisulfide) were prepared and their crystal structures characterized. The isomorphous complexes $[Ag(4\text{-PDS})_2 \cdot PF_6]$ **1** and $[Ag(4\text{-PDS})_2 \cdot ClO_4]$ **2** have twisted rhomboidal frameworks that consist of four Ag^I ions and four 4-PDS N-donor ligands, and show inclusion of the counter anions in their chiral cavities. The Ag^I ion has a tetrahedral coordination, and the rhomboidal units are assembled in the form of a 2-D sheet structure. The complex $[Ag(4\text{-PDS}) \cdot OTs]$ **3** (where OTs^- = *p*-toluenesulfonate) shows a 2-D sheet structure, constructed from 1-D zigzag chains bridged by interchain Ag–Ag interactions. The Ag^I ion has a T-shaped coordination environment, and the OTs^- anions are located between the sheets. The complex $[Ag(4\text{-PDS}) \cdot NO_3 \cdot (CH_3CN)_{0.5}]$ **4** is a 1-D zigzag coordination polymer with a chiral chain structure, incorporating acetonitrile as a guest molecule between the chains.

Introduction

The synthesis and characterization of supramolecular coordination compounds has been investigated extensively in the last decade.[1] These coordination compounds afford a variety of assembled structures and cavities, and also provide a reaction environment for guest molecules.[2] Although various metal ions are used for constructing coordination polymers, the Ag^I ion in particular is known to produce a variety of coordination environments such as linear, T-shaped, tetrahedral, and octahedral.[1d] When combined with bidentate ligands, this leads to various types of polymeric structures such as 1-D (linear chain,[3] zigzag chain,[4] helix,[5] stair-type,[6] ladder[7] and square mesh[8]), 2-D (honeycomb,[9] brick,[10] entanglement[11] and pillar[12]), and 3-D network[13] structures.

In order to realize coordination polymers with unique extended networks, we have combined the Ag^I ion with the bidentate ligand of 4,4′-dipyridyldisulfide (Scheme 1), abbreviated as 4-PDS, with various counter anions. The advantages of the 4-PDS ligand are that: i) the twisted structure, due to the –S–S– bridge, may lead to topologically interesting molecular assemblies; ii) the presence of the chalcogen moiety may lead to unique network structures[9] because of its bonding ability to soft metal ions; and in particular, iii) the twisted structure accompanies the axial chirality, generating the *P*- and the *M*-forms of optical antipodes, as shown in Scheme 1. Thus, the introduction of 4-PDS into coordination polymers is of special interest in terms of chiral crystal engineering, or for realizing optical properties[14] such as fluorescence or non-linear phenomena. We have recently reported on the complexation of the 4-PDS ligand with $M(hfac)_2$ (M = Cu, Mn, hfac = 1,1,1,5,5,5-hexafluoroacetylacetone), which afforded 1-D coordination polymers with helical or zigzag chain structures.[15] Kitagawa and co-workers have also reported on a coordination polymer with $Cd(NO_3)_2$.[16] We further combined the 4-PDS ligand with various Ag^I salts and obtained the following coordination polymers: $[Ag(4\text{-PDS})_2 \cdot PF_6]$ **1**; $[Ag(4\text{-PDS})_2 \cdot ClO_4]$ **2**; $[Ag(4\text{-PDS}) \cdot OTs]$ **3**; and $[Ag(4\text{-PDS}) \cdot NO_3 \cdot (CH_3CN)_{0.5}]$ **4**, that show various kinds of interesting network structures.



Scheme 1 Optical antipodes of 4,4′-dipyridyldisulfide (4-PDS).

Experimental

General methods

All reagents were commercially available. Infrared spectra were recorded on a JASCO FT-IR 230 spectrometer as KBr pellets for **1**, **3**, and **4**, and on a JASCO FT-IR 5300 spectrometer as a Nujol mull for **2** in the 4000–400 cm^{-1} range. Elemental analyses were performed by using a Yanagimoto C–H–N recorder (MT-3). Solid state UV-vis spectra were recorded on a JASCO V-570 UV/VIS/NIR spectrophotometer. Emission spectra were obtained on a SPEX FluoroMax spectrophotometer.

Preparations

$[Ag(4\text{-PDS})_2 \cdot PF_6]$ 1. To a solution of $AgPF_6$ (25 mg, 1.0 × 10^{-1} mmol) in 3 ml of water, a solution of 4,4′-dipyridyldisulfide (44 mg, 2.0 × 10^{-1} mmol) in 3 ml of methanol was added. A white powder precipitated immediately. After stirring for 30 min, the precipitate was filtered, and the white solid washed with water, acetone and diethyl ether, successively.

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Extraction of the solid with CH_3CN followed by evaporation under vacuum afforded a white solid of **1** (59 mg, yield 86%). X-Ray quality crystals were grown by slow evaporation of an CH_3CN solution at ambient temperature. FT-IR data (cm^{-1}): 3099m, 3050m, 1579s, 1543s, 1480s, 1411s, 1061s, 869s, 837s, 802s, 708s, 557s, 505s and 490s. Calc. for $C_{20}F_6H_{16}N_4PS_4Ag$: C, 34.64; H, 2.33; N, 8.08. Found: C, 34.67; H, 2.32; N, 8.17%.

[Ag(4-PDS)$_2$·ClO$_4$] 2. A procedure similar to that of **1** was employed. To a solution of $AgClO_4$ (21 mg, 1.0 × 10^{-1} mmol) in 3 ml of methanol, a solution of 4,4′-dipyridyldisulfide (44 mg, 2.0 × 10^{-1} mmol) in 3 ml of methanol was added. A white powder precipitated immediately. After stirring for 30 min the precipitate was filtered, and the white solid washed with methanol and diethyl ether, successively. Extraction of the solid with CH_3CN followed by evaporation under vacuum afforded a white powder of [Ag(4-PDS)$_n$·ClO$_4$] (33 mg, n = 1 or 2). X-Ray quality crystals of **2** (n = 2) could be grown by slow diffusion of diethyl ether into the product dissolved in CH_3CN at ambient temperature. FT-IR data (cm^{-1}): 1582s, 1416m, 1227m, 1076br, 812m, 714m, 619m and 488m. The powdered reaction product seems to contain mainly the 1 : 1 complex (n = 1). Calc. for $C_{10}ClH_8N_2O_4S_2Ag$: C, 28.08; H, 1.89; N, 6.55. Found: C, 28.89; H, 2.12; N, 7.51%.

[Ag(4-PDS)·OTs] 3. A procedure similar to that for **1** was employed. To a solution of AgOTs (28 mg, 1.0 × 10^{-1} mmol) in 3 ml of water, a solution of 4,4′-dipyridyldisulfide (22 mg, 1.0 × 10^{-1} mmol) in 3 ml of methanol was added. A white powder precipitated immediately. After stirring for 30 min the precipitate was filtered, and the white solid was washed with water, acetone and diethyl ether, successively. Extraction of the solid with CH_3CN followed by evaporation under vacuum afforded a white solid of **3** (35 mg, yield 70%). X-Ray quality crystals were grown by slow evaporation of an CH_3CN solution at ambient temperature. FT-IR data (cm^{-1}): 3084m, 3025m, 2451s, 1584s, 1543m, 1480s, 1417s, 1324m, 1220s, 1167s, 1118s, 1062s, 1006s, 814s, 712s, 679s, 568s and 491s. Calc. for $C_{17}H_{15}N_2O_3S_3Ag$: C, 40.88; H, 3.03; N, 5.61. Found: C, 40.93; H, 3.03; N, 5.66%.

[Ag(4-PDS)·NO$_3$·(CH$_3$CN)$_{0.5}$] 4. The procedure used was similar to that described for the preparation of **3**, except 17 mg (1.0 × 10^{-1} mmol) of $AgNO_3$ was used instead of AgOTs. A white solid of **4** was obtained in a yield of 86% (33 mg). X-Ray quality crystals were grown by slow diffusion of acetone into **4** dissolved in CH_3CN at ambient temperature. The crystal contained the acetonitrile molecule between the sheets with an occupancy of *ca.* 0.5 as determined by the X-ray analysis (P = 0.44). FT-IR data (cm^{-1}): 3032m, 2444w, 1575s, 1480m, 1359s, 1328s, 1219m, 1062m, 803s, 707m and 491s. Calc. for $C_{10}H_8N_3O_3S_2Ag$: C, 30.78; H, 2.07; N, 10.77. Found: C, 30.78; H, 2.07; N, 10.77%.

[Ag(4-PDS)·BF$_4$] 5. The procedure used was similar to that described for the preparation of **3**, except 20 mg (1.0 × 10^{-1} mmol) of $AgBF_4$ was used instead of AgOTs and the washing solvent was ethanol instead of acetone. The white solid of **5** was obtained in a yield of 76% (32 mg). FT-IR data (cm^{-1}): 3103m, 2451m, 1589s, 1487m, 1422s, 1230m, 1068s, 818m, 717m and 494m. Calc. for $BC_{10}F_4H_8N_2S_2Ag$: C, 28.94; H, 1.94; N, 6.75. Found: C, 28.86; H, 2.00; N, 6.74%.

Crystal structure analyses

All the X-ray data were collected using Mo-Kα radiation on a Rigaku AFC-5S four-circle diffractometer. Crystal data, data collection parameters and analysis statistics for **1**–**4** are listed in Table 1. Selected interatomic distances and angles are given in Table 2. All calculations were performed using the teXsan crystallographic software package.[17] These structures were solved by direct methods (SIR92[18] or SHELX-97[19]) and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically, and absorption correction was applied (ψ-scans). The acetonitrile molecule in **4** was found from the Fourier map, and the position was fixed during refinements. Though some of the hydrogen atoms could be located by the Fourier syntheses, all hydrogen atoms were inserted at the calculated positions using a rigid model.

CCDC reference numbers 172107–172110.

See http://www.rsc.org/suppdata/dt/b1/b106032p/ for crystallographic data in CIF or other electronic format.

Results and discussion

A. Two-dimensional coordination polymers with a rhomboidal framework: [Ag(4-PDS)$_2$·PF$_6$] 1 and [Ag(4-PDS)$_2$·ClO$_4$] 2

The molecular structure and coordination environment around the Ag^I ion in **1** are shown in Fig. 1(a), together with the atomic numbering scheme. Selected bond lengths and angles are listed in Table 2. Each 4-PDS unit acts as a bidentate ligand and exhibits a typical twisted conformation (*vide infra*). The Ag^I ion

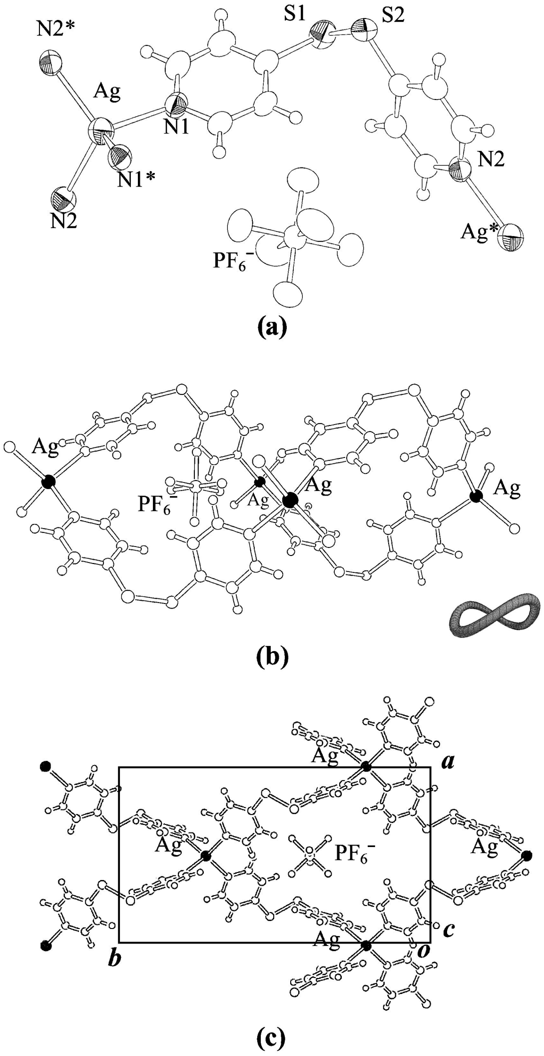


Fig. 1 (Top, a) An ORTEP[29] drawing of **1** with the atom numbering scheme, showing the silver coordination environment. Displacement ellipsoids are shown at the 50% probability level. (Middle, b) The twisted rhomboidal framework of **1**. Only one PF$_6^-$ counter anion is shown for clarity. Also shown is a schematic illustration of the framework. (Bottom, c) Packing diagram of **1** viewed along the *c*-axis. Only one PF$_6^-$ counter anion is shown for clarity.

Table 1 Crystallographic data for **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_{20}F_6H_{16}N_4PS_4Ag$	$C_{20}ClH_{16}N_4O_4S_4Ag$	$C_{17}H_{15}N_2O_3S_3Ag$	$C_{11}H_{9.5}N_{3.5}O_3S_2Ag$
Formula weight	693.45	647.93	499.37	410.71
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C_2/c	C_2/c	$P2_1/n$	$P2_1/c$
a/Å	11.068(6)	10.739(3)	10.611(6)	4.957(2)
b/Å	19.811(5)	19.527(1)	9.640(3)	19.291(3)
c/Å	11.485(6)	11.208(1)	18.684(3)	15.335(2)
β/°	95.30(4)	92.29(2)	94.06(2)	91.76(2)
V/Å^3	2507(1)	2348.4(7)	1906(1)	1465.6(7)
Z	4	4	4	4
μ(Mo-Kα)/cm^{-1}	12.62	13.62	14.02	16.67
T/K	296	100	296	296
Measured reflections	3121	2929	4888	3872
Observed reflections	2999	2816	4380	3373
R_1, R_w^{a}	0.039 0.120	0.030, 0.106	0.112, 0.305	0.096, 0.261

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2 Selected bond distances (Å) and angles (°), with esds in parentheses, for **1**–**4**

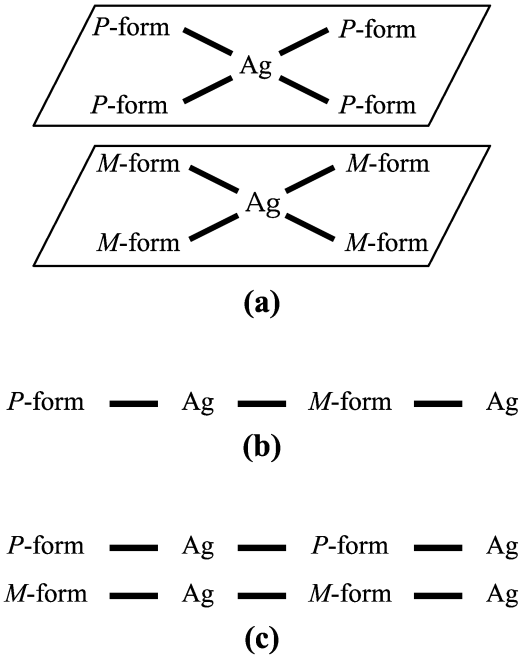
Complex **1**			
Ag–N(1)	2.333(3)	Ag–N(2)	2.297(3)
S(1)–S(2)	2.028(2)	N(1)–Ag–N(1^i)	106.1(1)
N(1)–Ag–N(2)	117.4(1)	N(2)–Ag–N(2^i)	109.7(1)
N(2)–Ag–N(1^i)	103.4(1)		
Complex **2**			
Ag–N(1)	2.318(2)	Ag–N(2^i)	2.282(2)
S(1)–S(2)	2.033(1)	N(1^i)–Ag–N(1^{ii})	107.8(1)
N(1^i)–Ag–N(2)	117.47(8)	N(2)–Ag–N(2^{iii})	115.6(1)
N(2)–Ag–N(1^i)	99.56(8)		
Complex **3**			
Ag–N(1^i)	2.175(8)	Ag–N(2^{ii})	2.167(8)
Ag–Ag(^{iii})	3.044(2)	S(1)–S(2)	1.984(6)
N(1)–Ag–N(2)	162.6(3)	N(1)–Ag–Ag(^{i})	102.1(2)
N(2)–Ag–Ag(^{i})	88.5(2)		
Complex **4**			
Ag–N(1)	2.139(9)	Ag–N(2)	2.145(8)
S(1)–S(2)	2.022(4)	N(1)–Ag–N(2)	166.2(4)

Symmetry codes used to generate equivalent atoms. For **1**: (i) $-x + 2, y, -z + 3/2$. For **2**: (i) $x - 1/2, y - 1/2, z$; (ii) $-x + 1/2, y - 1/2, -z + 1/2$; (iii) $-x, y, -z + 1/2$. For **3**: $-x + 1, -y, -z$; (ii) $-x + 1/2, y + 1/2, -z + 1/2$; (iii) $-x + 1, -y + 1, -z$.

in **1** shows tetrahedral coordination, in which the N(1)–Ag–N(2*) and N(1)–Ag–N(1*) angles are 117.4(1) and 106.1(1)°, and the Ag–N(1) and Ag–N(2*) bond lengths are 2.333(3) and 2.297(3) Å, respectively. A local coordination environment scheme similar to that found in [{Ag(pyz)$_3$}(BF$_4$)] (pyz = pyrazine).[20] Complex **2**, with a slightly smaller ClO_4^- counter anion, is isomorphous with **1**. The coordination geometries are almost comparable for both complexes, as shown in Table 2.

Fig. 1(b) shows the unique twisted rhomboidal framework of **1** formed by the four 4-PDS ligands and the four Ag^I ions. Interestingly, the shape of the unit is somewhat analogous to a Möbius strip, as schematically illustrated in the figure. The rhomboidal cavity accommodates two PF_6^- counter anions. The units are further interconnected and extend as a 2-D sheet, as shown in Fig. 1(c). It is noteworthy that the cavity is a chiral one, consisting only of either the *M*- or *P*-form of the ligand. Thus the assembled 2-D sheet is chiral, as schematically shown in Scheme 2(a), although the structures of **1** and **2** have a centre of symmetry (space group *C*2/*c*) and show no chirality. The centrosymmetry of the crystals originates from alternate stacking of sheets with opposite chirality.

The coordination environment around the Ag^I ion in these complexes bears some resemblance to that in [{Ag$_2$(bpethy)$_5$}(BF$_4$)$_2$] (bpethy = 1,2-bis(4-pyridyl)ethyne),[11] although the bpethy complex has a square cavity structure because of the linear shape of the ligand. Thus, the formation of the unique twisted cavity in the present case can be understood in terms of the characteristic torsion of the 4-PDS ligand. Indeed, coordination polymers of [Cd(py–X–py)$_2$·(NO$_3$)$_2$] (py = 4-pyridyl, X = CH$_2$ or C=CH$_2$)[21] and [Cd(4-PDS)$_2$(H$_2$O)$_2$]·2NO$_3$·2EtOH·2H$_2$O,[16] formed by more flexible ligands, show flat cavities.



Scheme 2 Schematic illustration of the chirality and structures of coordination polymers from 4-PDS and Ag^I ions: (a) for **1** and **2**, (b) for **3**, and (c) for **4**.

B. A two-dimensional coordination polymer formed by the interchain Ag–Ag interactions: [Ag(4-PDS)·OTs] 3

The molecular structure and the coordination environment around the Ag^I ion in **3** are shown in Fig. 2(a), together with the atomic numbering scheme. Selected bond lengths and angles are listed in Table 2. Fig. 2(b) shows the 2-D sheet structure of **3**, constructed from 1-D zigzag chains bridged by interchain Ag–Ag interactions. The Ag^I ion has a T-shaped coordination, with N(1)–Ag–N(2) and N(1)–Ag–Ag* bond angles of 162.6(3) and 102.1(2)°, and Ag–N(1), Ag–N(2), and Ag ··· Ag* distances of 2.175(8), 2.167(8), and 3.044(2) Å, respectively. Fig. 2(c) shows the packing structure of **3** including the OTs$^-$

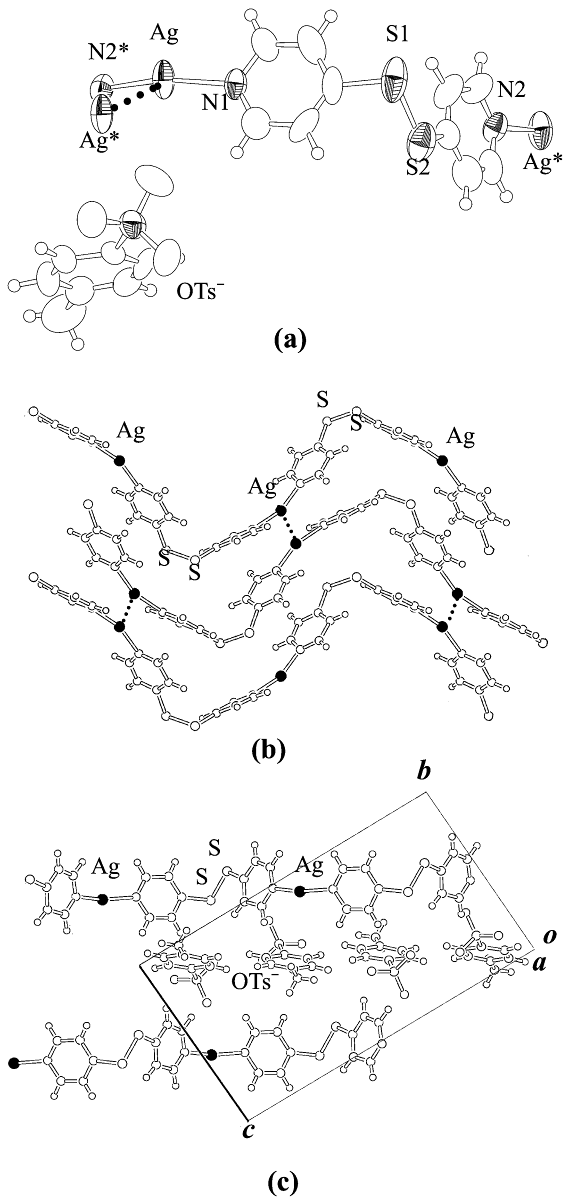


Fig. 2 (Top, a) An ORTEP drawing of **3** with the atom numbering scheme, showing the silver coordination environment. Displacement ellipsoids are shown at the 50% probability level. (Middle, b) The 2-D sheet structure of **3**. (Bottom, c) Packing diagram of **3** viewed along the *b*-axis. The OTs$^-$ anions are omitted for clarity.

counter anions. These anions are located between the sheets, with the molecular planes oriented parallel to the 2-D sheet of the coordination polymers. From the viewpoint of chirality, the 1-D unit consists of alternate linkages of the *M*- and *P*-forms of the ligands with the Ag^{I} ions. The chain is thus represented as –*M*–(Ag)–*P*–(Ag)–*M*–(Ag)–*P*–, as schematically shown in Scheme 2(b), resulting in an achiral structure with centrosymmetric space group $P2_1/n$.

A local coordination environment of Ag^{I} similar to that exhibited in **3** is found in [Ag(bpp)·OTf·EtOH] (where bpp = 1,3-bis(4-pyridyl)propane, OTf = trifluoromethanesulfonate). The Ag^{I} ··· Ag^{I} distances of several coordination polymers retrieved from the Cambridge Structure Database are compared in Table 3, in order of increasing bond distance. Although the nature of the interactions is not fully understood, Ag ··· Ag distances of 2.50–3.00 Å are considered to originate from weak d^{10}–d^{10} aurophilic interactions.[22] Even in compounds with longer Ag ··· Ag distances, *e.g.*, [Ag(NO$_3$)$_3$-(py$_2$S)$_2$·2H$_2$O], an Ag ··· Ag distance shorter than for other interactions, such as S ··· S or π–π, is claimed to be indirect evidence of Ag ··· Ag interactions.[23] Solid state UV-Vis absorption measurement showed that **3** has a small absorption band at 425 nm, and a fluorescence is observed at 600 nm when this band is excited. As reported by Che and co-workers, the absorption and the fluorescence properties may originate from the d^{10}–d^{10} interaction.[24] This interpretation is further supported by the fact that no fluorescence was observed for complexes **1**, **2**, and **4**, which have no Ag ··· Ag interactions.

C. A one-dimensional coordination polymer with a simple zigzag chain structure: [Ag(4-PDS)·NO$_3$·(CH$_3$CN)$_{0.5}$] 4

The molecular structure and the coordination environment around the Ag^{I} ion in **4** are shown in Fig. 3(a), together with the atomic numbering scheme. Selected bond lengths and angles are listed in Table 2. This is a simple 1-D zigzag coordination polymer, as shown in Fig. 3(b). Each Ag^{I} ion is coordinated by two N atoms from the 4-PDS ligand in a linear geometry in which the Ag–N(1), Ag–N(2) bond distances and the N(1)–Ag–N(2) bond angle are 2.139(9) and 2.145(8) Å and 166.2(4)°, respectively.

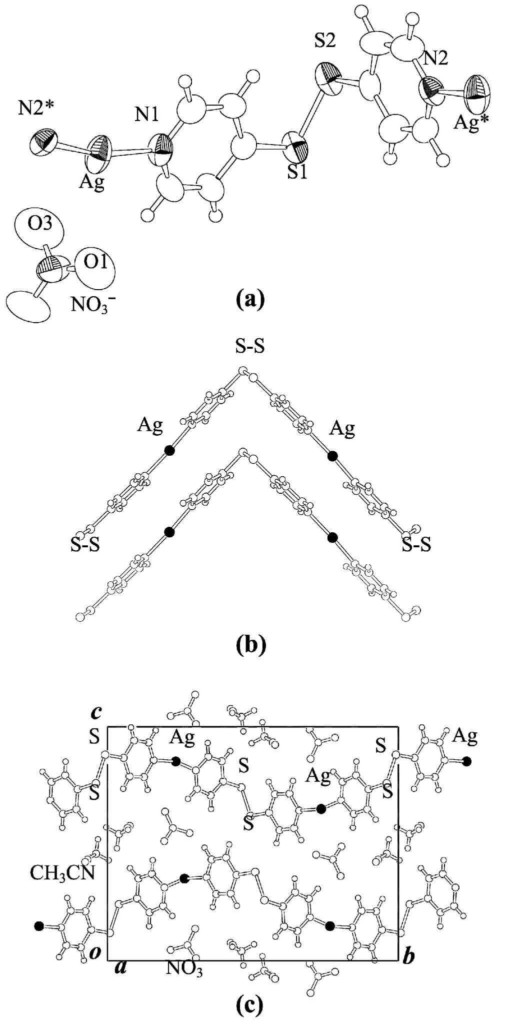


Fig. 3 (Top, a) An ORTEP drawing of **4** with the atom numbering scheme, showing the silver coordination environment. Displacement ellipsoids are shown at the 50% probability level. (Middle, b) The 1-D zigzag chain of **4**. (Bottom, c) Packing diagram of **4** viewed along the *a*-axis.

Fig. 3(c) shows the packing structure of **4**, and includes the counter anion and CH$_3$CN molecules, which are interposed between the chains. Although the NO$_3$$^-$ anion is located beside the Ag^{I} ion, there seems to be no coordination bond between them since the Ag ··· O(3) distance of 2.86(2) Å is a little longer than a typical Ag ··· O interaction distance.[4,5a,9,22a,25]

Table 3 Ag ··· Ag distances (Å) in several Ag^{I} coordination polymers

Compound[a]	Ag ··· Ag distance/Å	Ref.
[Ag(4,4′-bpy)·NO$_3$]	2.78(1)	22*a*
[Ag(4,4′-bpy)·NO$_3$]	2.970(2)	13*b*
[Ag(4-PDS)·OTs]	3.044(2)	This work
[Ag$_2$(tren(mim)$_3$)]$_n$(NO$_3$)$_{2n}$·nH$_2$O	3.053(1)	3*a*
[Ag(bpp)·OTf·EtOH]	3.089(1)	5*d*
[Ag(2,4′-bpy)·ClO$_4$]	3.1526(6)	5*b*
[Ag(pydz)$_2$·BF$_4$]	3.282(1)	5*a*
[Ag(3,3′-dcpa)·OTf·C$_6$H$_6$]	3.377(1)	22*b*
[Ag$_3$(NO$_3$)$_3$(Py$_2$S)$_2$·2H$_2$O]	3.436(2)	23

[a] bpy = bipyridine, OTs = *p*-toluenesulfonate, tren(mim)$_3$ = tris{2-[2-(1-methyl)imidazolyl]methyliminoethyl}amine, bpp = 1,3-bis(4-pyridyl)propane, OTf = trifluoromethanesulfonate, pydz = pyridazine, 3,3′-dcpa = 3,3′-dicyanodiphenylacetylene, py$_2$S = 4,4′-bispyridylsulfide.

Each 1-D chain unit is chiral, and is represented by either –*M*–(Ag)–*M*–(Ag)–*M*–(*M*-chain) or –*P*–(Ag)–*P*–(Ag)–*P*–(*P*-chain), as schematically shown in Scheme 2(b). The complex consists of a 1 : 1 ratio of *P*- and *M*-chains, and is achiral with a centrosymmetric space group ($P2_1/c$).

A local coordination environment similar to that exhibited in complex **4**, is found in [Ag(4-bpbd)NO$_3$·CH$_3$CN] (4-bpbd = 1,4-bis(4-pyridyl)butadiyne).[26] Complex **4** shows no significant interaction between the chains; the interchain distances of Ag ··· Ag, Ag ··· O(2*) and S(1) ··· S(1*) are *ca.* 4.9, 3.37(1), and 3.73 Å, respectively, which are longer than the usual contact distances encountered. This contrasts with the py–S–py bridged coordination polymer [Ag$_3$(NO$_3$)$_3$(py$_2$S)$_2$·2H$_2$O], which shows several interchain interactions, such as Ag ··· Ag and π–π type.[23]

D. Assembled structures of 4-PDS coordination polymers

The Ag^{I} complexes with 4-PDS are found to display interesting assembled structures and dimensionalities as shown above, in contrast to the relatively simple 1-D coordination polymers of [4-PDS·M(hfac)$_2$], on which we have reported previously.[15] We have assumed that the coordinational variation of Ag^{I} as well as the presence of counter anions has led to the structural variety in the present complexes. It is known that the crystal structures of coordination polymers are highly influenced by the shape of the counter anion, which may act as the template of the coordination polymer. For example, the anion dependence of the coordination polymer assembly for the complex from Ag^{I} and bpsb (= 1,2-bis[(2-pyrimidinyl)sulfanylmethyl]benzene) has been demonstrated by Hong and co-workers.[9] We speculate that the counter anions may serve as a template in the formation of complexes **1** and **2**, producing the Möbius-strip-like cavity accommodating the anions.

We next focus on the conformation of the 4-PDS ligand. The bpe (= 1,2-bis(4-pyridyl)ethane) ligand, bearing the –CH$_2$–CH$_2$– bridging group, is more flexible than 4-PDS, thus the ligand conformation of bpe is highly affected by intermolecular interactions.[27] In contrast, the 4-PDS ligand maintains its characteristic conformation as described above, despite the difference in the coordination schemes. The S–S bond length and the C–S–S–C torsion angles in 4-PDS existing in the present complexes are listed in Table 4, together with those for [4-PDS·M(hfac)$_2$] $_2$ (M = Cu, Mn). These values are very close to the typical values found in aromatic disulfides,[28] regardless of the metal species, coordination environment, and counter anion. Thus, the disulfide moiety is shown to be rather rigid, maintaining its characteristic shape even when coordinated to metal ions. This characteristic has produced the structural uniqueness of the present compounds.

Table 4 S–S distances (Å) and C–S–S–C torsion angles (°) in 4-PDS ligands in several coordination polymers

Compound	S–S distance/Å	C–S–S–C torsion angle/°
1	2.028(2)	91.4(2)
2	2.033(1)	89.7(1)
3	1.984(6)	95.5(8)
4	2.022(4)	83.8(6)
[4-PDS·Cu(hfac)$_2$][a]	2.029(2)	88.1(2)
[4-PDS·Mn(hfac)$_2$][a]	2.031(5)	91.6(6)

[a] Ref. 15.

The most interesting feature of the present system is the chirality of the ligand and its consequence for the assembled structures. The chirality of the present complexes is schematically shown in Scheme 2. It is interesting to note that, as described above, chiral structural units are found as a 2-D sheet in **1** and **2**, and as a 1-D chain in **4**. In M(hfac)$_2$ complexes, [4-PDS·Cu(hfac)$_2$] shows 1-D chiral chains, similar to complex **4**, whereas [4-PDS·Mn(hfac)$_2$] shows 1-D achiral chains, similar to **3**. The complex [Cd(4-PDS)$_2$(H$_2$O)$_2$]·2NO$_3$·2EtOH·2H$_2$O[16] has an achiral 1-D chain structure. Thus, all the complexes so far obtained are achiral crystals, with centrosymmetric space groups. From these comparisons, a general structural correlation is found for the system: when the 1-D chain unit is achiral, represented as –*P*–(M)–*M*–(M)–*P*–, it forms a zigzag chain structure as exhibited by **3** and [4-PDS·Mn(hfac)$_2$], while complexes with chiral chains form a helical chain structures such as exhibited by **4** and [4-PDS·Cu(hfac)$_2$]. The twisted structure of the chiral cavities in **1** and **2** is also ascribable to be the consequence of the axial chirality of the bridging ligand.

In conclusion, we have prepared coordination polymers from Ag^{I} and 4-PDS, demonstrating the dimensionality from 1-D to 2-D structures. This study also showed that the twisted ligand is interesting from the viewpoint of asymmetrical crystal engineering. As we could obtain 1-D and 2-D chiral structural units in this study, the construction of a chiral crystal seems to be feasible, the structure and physical properties of which would be highly intriguing.

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