

Tuning the framework formation of silver(I) coordination architectures with heterocyclic thioethers

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The reactions of a series of nitrogen-containing heterocyclic thioether ligands, 2,2'-[methylenebis(thio)]bis(pyrimidine) (**L**¹), 2,2'-[1,2-ethanediy]bis(thio)]bis(pyrimidine) (**L**²), 2,2'-[methylenebis(thio)]bis[5-methyl-1,3,4-thiadiazole] (**L**³) and 2,2'-[1,2-ethanediy]bis(thio)]bis[5-methyl-1,3,4-thiadiazole] (**L**⁴), with silver(I) nitrate or silver(I) perchlorate salt led to the formation of five new metal–organic supramolecular architectures from dinuclear to three-dimensional structures. All the structures were determined by single-crystal X-ray diffraction analysis. In the crystal structures of the five complexes, a variety of coordination modes of Ag^I have been observed, probably due to the variation of the chain length of the linker unit or the terminal groups as well as the counter anions, which indicates that the nature of the ligands is a determining factor in controlling the structural topologies of such metal–organic supramolecular architectures. Geometrical effects seem to be more important than electronic effects in these systems, leading the Ag^I centre to prefer to coordinate to N donors first rather than S donors despite Ag^I being a 'soft' metal.

Introduction

The rational design of coordination architectures based on multitopic organic ligands and metal centres represents one of the most exciting and rapidly developing fields in current coordination and supramolecular chemistry owing to their potential as functional materials.^{1–3} Bridging ligands take an important role in adjusting the coordination frameworks, and the alternation of the geometry of the linker unit or the nature of the coordinating donor may lead to the formation of different frameworks with tailored properties and functions. There has been rapid development of multi-dimensional networks based primarily on linking metal centres with rigid bridging components such as 4,4'-bipyridine,⁴ and some extended architectures or networks constructed from flexible bridging units have also been reported, although such examples are still comparatively rare.⁵

Ag^I is a favorable and fashionable building block or connecting node for coordination polymers,⁶ and it has been classified as an extremely soft acid that favors coordination to soft bases such as S and unsaturated N-containing ligands. However, fully characterized examples of the coordination complexes of N-containing heterocyclic thioether ligands with Ag^I ions are mainly restricted to pyridine derivatives, and a small number of examples with other heterocyclic thioether ligands have been reported.^{4,7,8} The ligands containing pyrimidinyl or thiodiazole group have shown interesting coordination chemistry with transition metal ions⁸ and thus, their complexes with Ag^I may give interesting results due to their potential for the construction of coordination architectures.

We report herein the construction of a series of Ag^I coordination architectures forming different frameworks, from dinuclear to three-dimensional structures, by using nitrogen-containing heterocyclic dithioether ligands as building blocks. The four ligands we selected or designed in this study, 2,2'-[methylenebis(thio)]bis(pyrimidine) (**L**¹), 2,2'-[1,2-ethanediy]bis(thio)]bis(pyrimidine) (**L**²), 2,2'-[methylenebis(thio)]bis[5-methyl-1,3,4-thiadiazole] (**L**³) and 2,2'-[1,2-ethanediy]bis(thio)]bis[5-methyl-1,3,4-thiadiazole] (**L**⁴) are closely related to each other in structure (see Chart 1). We are attempting to examine the influence of terminal groups and chain length of the linker unit of the ligands as well as the counter anions on the resultant structures of their Ag^I complexes. The crystal structures of these complexes were elucidated by X-ray diffraction analyses and the distinction of the coordination modes of

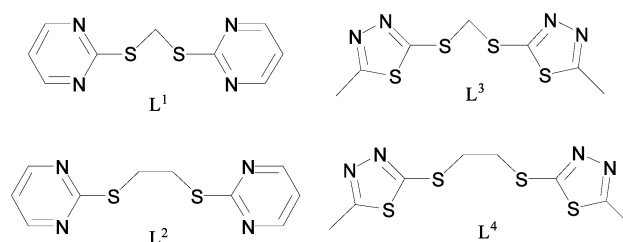


Chart 1

Ag^I was discussed. Crystallographic data and experimental details for structural analyses of all the five complexes are summarized in Table 1.

Results and discussion

One-dimensional chain of [AgL¹NO₃]_n, 1

In complex **1**, each Ag^I ion has a slightly distorted trigonal planar geometry comprised of two pyrimidine N donors from different ligands and an O donor from the nitrate counter anion. All three silver–donor bond distances (see Table 2) are within the range expected for such coordination bonds.⁹ The Ag^I centre deviates from the coordination plane by 0.0939(7) Å, and the two N–Ag–O and the N–Ag–N bond angles are 120.2(1), 87.9(2) and 131.2(1)°, respectively.

In **1**, each **L**¹ ligand bridges two Ag^I centres with two N donors from different pyrimidine rings, and the one-dimensional chain consisting of [AgL¹NO₃]_n units along the crystallographic *b*-direction is formed by the action of the 2₁ screw axis (Fig. 1a). The ligand-bridged Ag ⋯ Ag nonbonding distance is 8.826(4) Å. The mean planes of these two pyrimidine rings are inclined to one another with a dihedral angle of 47.5(2)°. It should be noted that only one of the N atoms of 2-thiopyrimidine takes part in coordination, and the S atom does not coordinate to the Ag^I centre, which is not similar to other silver complexes with the derivatives of pyrimidine-2-thiolate.¹⁰ The shortest distance between Ag and S is 3.27(3) Å, which is out of the range expected for such coordination bonds.^{10,11}

The Ag^I centre in one chain shows weak interactions with two S atoms of another adjacent chain (the average Ag ⋯ S distance is 3.04(2) Å), and these weak interactions link the 1D chains into pairs as depicted in Fig. 1b. The distance between

Table 1 Crystallographic data and structural refinement summary for complexes 1–5

	1	2	3	4	5
Chemical formula	C ₉ H ₈ AgN ₅ O ₃ S ₂	C ₂₀ H ₂₀ Ag ₂ N ₁₀ O ₆ S ₄	C ₇ H ₁₀ AgN ₅ O ₄ S ₄	C ₈ H ₁₀ Ag ₂ N ₆ O ₆ S ₄	C ₁₆ H ₂₁ Ag ₂ Cl ₂ N ₈ O ₈ S ₆
Formula weight	406.19	840.44	464.31	630.20	932.41
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	7.431(3)	24.75(1)	13.831(5)	13.641(6)	8.23(2)
<i>b</i> /Å	8.826(3)	8.267(4)	18.293(6)	8.579(4)	13.30(3)
<i>c</i> /Å	10.210(4)	16.055(8)	8.351(3)	16.480(7)	15.49(3)
<i>a</i> °	90	90	90	90	78.25(4)
<i>β</i> °	106.562(6)	123.818(8)	122.308(5)	107.818(8)	83.02(4)
<i>γ</i> °	90	90	90	90	84.41(4)
<i>V</i> /Å ³	641.9(4)	2729(2)	1786(1)	1836(1)	1644(7)
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)	293(2)
<i>Z</i>	2	4	4	4	2
μ (Mo-K α)/mm ⁻¹	1.909	1.800	1.613	2.627	1.786
No. unique data (<i>R</i> _{int})	1860 (0.016)	2304 (0.040)	1528 (0.037)	3244 (0.096)	5153 (0.078)
No. measured reflections	2651	5227	3521	7304	5574
<i>R</i> ^a / <i>wR</i> ^b	0.0232/0.0442	0.0399/0.0901	0.0388/0.0864	0.0471/0.0739	0.0888/0.1985

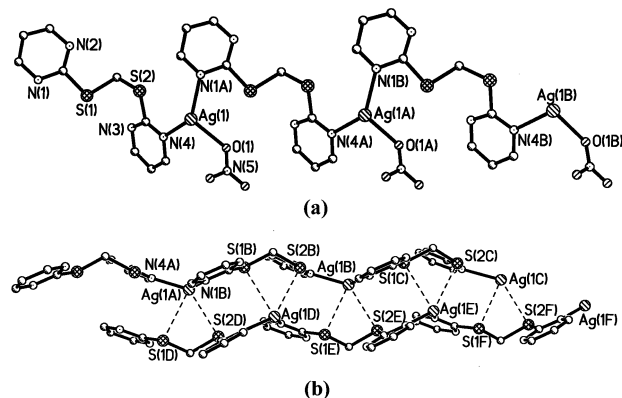
^a $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^b $wR = [\Sigma(|F_o|^2 - |F_c|^2)^2/\Sigma(F_o^2)]^{1/2}$.

Table 2 Selected bond lengths (Å) and angles (°) for complex 1

Ag(1)–N(1A)	2.318(4)	Ag(1)–N(4)	2.354(4)
Ag(1)–O(1)	2.434(4)		
N(1A)–Ag(1)–N(4)	131.2(1)	N(1A)–Ag(1)–O(1)	120.2(1)
N(4)–Ag(1)–O(1)	87.9(2)		

Table 3 Selected bond lengths (Å) and angles (°) for complex 2

Ag(1)–N(3A)	2.282(4)	Ag(1)–O(2)	2.378(5)
Ag(1)–S(1)	2.781(2)	Ag(1)–S(2)	2.814(2)
N(3A)–Ag(1)–O(2)	128.3(2)	N(3A)–Ag(1)–S(1)	98.3(1)
O(2)–Ag(1)–S(1)	133.0(1)	N(3A)–Ag(1)–S(2)	95.0(1)
O(2)–Ag(1)–S(2)	92.2(1)	S(1)–Ag(1)–S(2)	75.8(1)

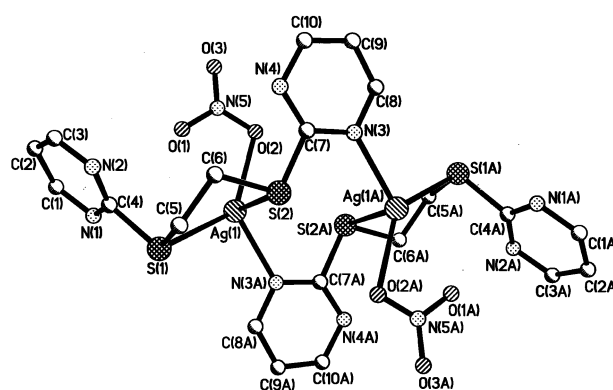
**Fig. 1** (a) The 1D chain of 1 and (b) pair chains formed by the weak interactions of Ag⁺...S (symmetry codes: A: *x* – 1, *y* – 1, *z*; B: *x* – 1, *y*, *z*; C: *x* – 1, *y* + 1, *z*; D: 1 – *x*, *y* – 1/2, 1 – *z*; E: 1 – *x*, *y* + 1/2, 1 – *z*; F: 1 – *x*, *y* + 3/2, 1 – *z*).

the parallel neighboring aromatic rings of the distinct chains is *ca.* 3.4 Å, indicating the presence of face-to-face π – π stacking interactions¹² along the crystallographic *a*-direction.

Dinuclear structure of [AgL²NO₃]₂, 2

Complex 2 is a centrosymmetric Ag₂L₂ dinuclear structure (Fig. 2) and the geometry of the Ag^I centre is a slightly distorted tetrahedron comprised of two S donors from one L² ligand, one N donor from another ligand and one O donor from the nitrate ion, with all four silver–donor bond distances within the range expected for such coordination (see Table 3).⁹

The coordination of two S atoms of the same ligand to Ag^I centre forms a five-membered chelate ring which adopts a

**Fig. 2** View of the dinuclear structure of 2 (symmetry code: $-x + 1/2, -y + 3/2, -z + 1$).

half-chair conformation with the S...S non-bonding distance of 3.44(3) Å. At the same time, an eight-membered centrosymmetric dinuclear ring which adopts a chair conformation is formed by the coordination of a N atom and a S atom from two distinct ligands to each of the two Ag^I centres, with the Ag...Ag separation of 4.46(4) Å. The planes of the pyrimidine rings located at the symmetric site are parallel to each other, while the two pyrimidine ring planes of the same ligand are inclined to each other at an angle of 77.1(3)°. Two nitrate counter ions are stretched to the opposite directions.

L¹ and L² just differ in the chain length of the linker unit, but L¹ acts as a bridging ligand while L² acts as both a bridging and a chelating ligand, resulting in very different coordination modes of the terminal group 2-thiopyrimidine and different structures of their complexes. Four-membered rings that would be formed by the two S donors coordinating to the Ag^I centre in L¹ are more geometrically strained than the corresponding five-membered rings that would be formed in L², and therefore, S donors do not coordinate to the Ag^I centre in L¹ while they do coordinate in L² to form the five-membered chelate rings.

One-dimensional chain of {[AgL³(NO₃)(H₂O)]_n, 3

Complex 3 shows a one-dimensional chain structure. The geometry of the Ag^I centre is a slightly distorted tetrahedron comprised of four N donors from four different thiadiazole rings of three distinct L³ ligand. The Ag–N bond distances are 2.338(4) and 2.364(4) Å (see Table 4), which are similar with those found in the complexes formed by the coordination of Ag^I and nitrogen-containing heterocyclic ligands.^{7,10}

In 3, one L³ ligand connects three Ag^I centres with four distinct N donors to form a –Ag–N–N–Ag–N–N–Ag– linear

Table 4 Selected bond lengths (Å) and angles (°) for complex **3**

Ag(1)–N(1)	2.364(4)	Ag(1)–N(2B)	2.338(4)
N(2B)–Ag(1)–N(2C)	119.0(2)	N(2B)–Ag(1)–N(1A)	103.6(1)
N(2C)–Ag(1)–N(1A)	114.5(1)	N(2B)–Ag(1)–N(1)	114.5(1)
N(2C)–Ag(1)–N(1)	103.6(1)	N(1A)–Ag(1)–N(1)	100.4(2)

structural unit along the *c*-direction with the Ag^I···Ag non-bonding distance of 4.23(1) Å (Fig. 3a). Ag(1) lies on a twofold axis, as does N(3)–O(2) of the nitro group, and C(4B). Two N atoms [N(2B) and N(2C)] from different thiadiazole rings of one ligand coordinate to the Ag^I centre, forming an eight-membered chelating ring. Two nitrogen atoms of one thiadiazole ring bridge two Ag atoms [Ag(1)–N(1)–N(2)–Ag(1A)] and two such bridges form a six-membered centrosymmetric dinuclear ring, with the two thiadiazole rings parallel to each other. Only one C atom in the linker unit forces the mean planes of two thiadiazole rings of one ligand inclined to one another at an angle of 61.4(2)°, resulting in two different kinds of six-membered rings, which are almost perpendicular to each other, with the dihedral angle of 84.9(2)°. All these six-membered rings adopt very flattened chair conformations and indeed are almost planar.

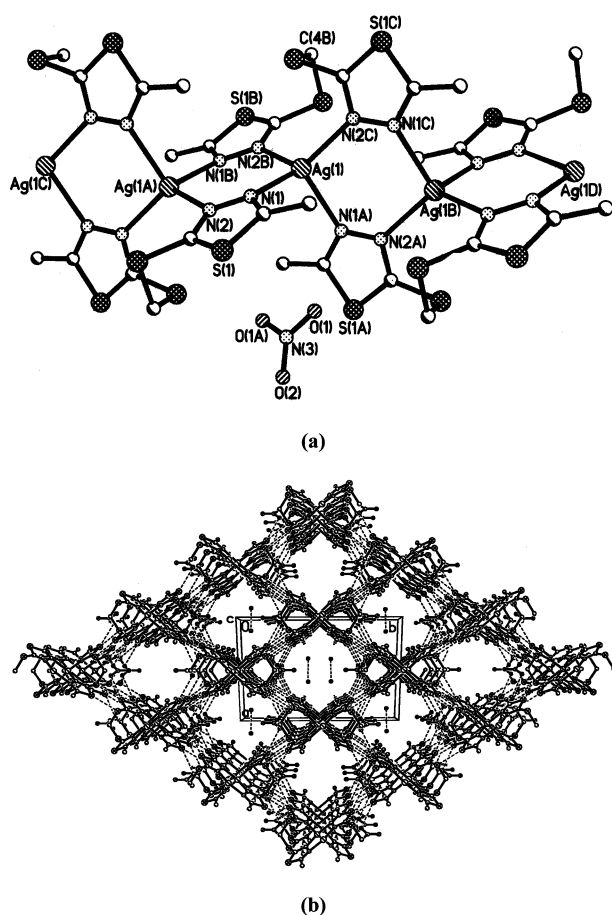


Fig. 3 (a) The 1D structure of **3** and (b) the 3D network formed by the weak interactions of S···S (symmetry codes: A: $x, 1 - y, 1 - z$; B: $x, 1 - y, -z$; C: $x, y, z + 1$; D: $x, y, z - 1$).

In the one-dimensional chain structure of **3**, only N atoms of the thiadiazole rings coordinate to Ag^I centre, and the exposed S atoms in the thiadiazole rings of distinct chains are connected through relatively weaker coordination interactions to form an infinite three-dimensional structure, as depicted in Fig. 3b, with the nitrate counter ions and the water molecules encapsulated inside the channel of the network. The S···S contact of 3.55(4) Å is less than the sum of the van der Waals radii of two

Table 5 Selected bond lengths (Å) and angles (°) for complex **4**

Ag(1)–N(2)	2.285(7)	Ag(1)–N(1A)	2.332(8)
Ag(1)–N(4)	2.343(7)	Ag(1)–O(4)	2.454(9)
Ag(2)–N(3B)	2.281(8)	Ag(2)–O(1)	2.478(7)
Ag(2)–S(3)	2.496(3)	Ag(2)–Ag(2B)	2.995(2)
N(2)–Ag(1)–N(1A)	123.3(3)	N(2)–Ag(1)–N(4)	113.0(3)
N(1A)–Ag(1)–N(4)	107.0(3)	N(2)–Ag(1)–O(4)	116.7(3)
N(1A)–Ag(1)–O(4)	95.5(3)	N(4)–Ag(1)–O(4)	97.2(3)
N(3B)–Ag(2)–O(1)	93.1(3)	N(3B)–Ag(2)–S(3)	151.9(2)
O(1)–Ag(2)–S(3)	114.9(2)	N(3B)–Ag(2)–Ag(2B)	84.1(2)
O(1)–Ag(2)–Ag(2B)	121.8(2)	S(3)–Ag(2)–Ag(2B)	83.9(1)

S atoms and such weak interactions can also be observed in other multi-sulfur systems.¹³

Three-dimensional network of [Ag₂L⁴(NO₃)₂]_n, **4**

Complex **4** is a three-dimensional network and shows two different central Ag^I centres (Fig. 4a). Selected bond lengths and angles are given in Table 5. Ag(1) adopts a slightly distorted tetrahedral geometry comprised of three N donors from three different thiadiazole rings of three distinct ligands and one O donor from a nitrate ion. Two Ag^I centres [Ag(1) and Ag(1A)] linked by N–N bridges of two thiadiazole rings of two distinct L⁴ ligands form a six-membered centrosymmetric dinuclear cyclic unit (unit A), which is as same as in **3**, with the Ag···Ag distance of 3.565(4) Å. This distance is slightly longer than the van der Waals contact distance for Ag–Ag (3.40 Å),¹⁴ illustrating the lack of direct metal–metal interaction. Ag(2) adopts a distorted trigonal planar geometry comprised of a S atom, a N atom from distinct ligands and an O donor from the nitrate ion. Two tri-coordinated Ag^I centres [Ag(2) and Ag(2B)] linked by S–C–N bridges of two terminal groups of two distinct ligands form an eight-membered metallocyclic unit (unit B), which adopts a chair conformation. In this unit, two Ag^I atoms interact with each other with the Ag–Ag distance of 2.995(4) Å, and similar Ag–Ag interactions have been observed in the complexes of other nitrogen-containing heterocyclic thioether ligands.¹⁵

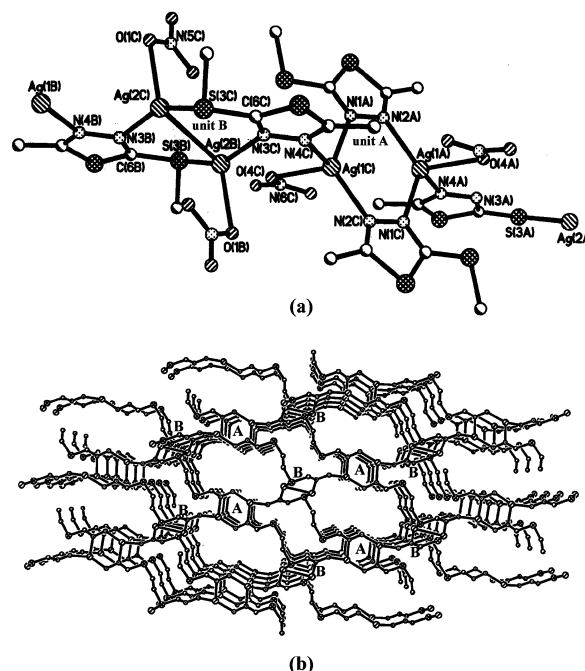


Fig. 4 (a) The two different coordination modes of Ag^I in **4** and (b) view from *b*-axis showing the 3D structure of **4** (only the skeleton of the structure and N atoms coordinated to Ag in thiadiazole rings are present and all the nitrate anions and irrelevant atoms are omitted for clarity) (symmetry codes: A: $x - 1, 1.5 - y, -z + 0.5$; B: $1 - x, 1.5 - y, -z + 0.5$; C: $-x + 1, y - 0.5, -z + 0.5$).

Table 6 Selected bond lengths (Å) and angles (°) for complex **5**

Ag(1)–N(8)	2.14(2)	Ag(1)–N(6)	2.24(1)
Ag(1)–N(4)	2.29(1)	Ag(1)–N(2)	2.29(1)
Ag(2)–N(7)	2.15(2)	Ag(2)–N(3)	2.23(1)
Ag(2)–N(1)	2.28(1)	Ag(2)–N(5)	2.30(1)
N(8)–Ag(1)–N(6)	119.1(5)	N(8)–Ag(1)–N(4)	120.5(5)
N(6)–Ag(1)–N(4)	92.4(4)	N(8)–Ag(1)–N(2)	117.1(5)
N(6)–Ag(1)–N(2)	98.9(5)	N(4)–Ag(1)–N(2)	104.3(4)
N(7)–Ag(2)–N(3)	119.6(6)	N(7)–Ag(2)–N(1)	113.4(6)
N(3)–Ag(2)–N(1)	103.1(5)	N(7)–Ag(2)–N(5)	116.8(6)
N(3)–Ag(2)–N(5)	100.2(5)	N(1)–Ag(2)–N(5)	101.2(5)

Each L^4 ligand uses one of its thiadiazole rings to bridge two Ag^I centres to form unit **A**, and the other 2-thiothiadiazole group to bridge two Ag^I centres to form unit **B**. Both kinds of metalocyclic units are arranged alternately in the crystal structure, with one unit **A** connecting four unit **B**s and one unit **B** connecting four unit **A**s from four different directions, exhibiting a 3D network generated by a 2_1 axis, a slide plane and an inversion centre (Fig. 4b).

L^3 and L^4 only differ in the chain length of the linker units, just like L^1 and L^2 , and the chain length has also a great effect on the coordination modes of the terminal group and the structures of the complexes. The geometrical strain force produced in the four-membered rings which would be formed by coordinations of S donors to the Ag^I centre in L^3 results in only N donors coordinating to Ag^I centre, and the coordination modes in complex **4** are more complicated due to the more linking carbon atoms. Thus, it should be concluded that more carbons in the linker unit would largely increase the flexibility and variety of the coordination modes of the terminal groups and the complexity of the structures.

We also noted that in L^1 (or L^2), only one N donor of the terminal group 2-thiopyrimidine coordinates to Ag^I centre, while in L^3 (or L^4), two N donors of the terminal group thiadiazole can coordinate to Ag^I centre. This indicates that the structure of the terminal group and the environment of the donors may greatly influence the structure construction.

One-dimensional chain consisting tetranuclear units of $\{[Ag_2L^{1,5}(CH_3CN)_2](ClO_4)_2\}_n$, **5**

Complex **5** is a one-dimensional coordination polymer consisting of $[Ag_4L^4(CH_3CN)_4]^{4+}$ cations and ClO_4^- ions. The geometry at the Ag^I centre is a slightly distorted tetrahedron comprised of three N donors from three thiadiazole rings of three distinct L^4 ligands and a N atom of an acetonitrile molecule. The four silver–nitrogen bond distances range from 2.14(2) to 2.30(1) Å, among which the distances between Ag and N of acetonitrile are slightly shorter, owing to the greater electronegativity of acetonitrile molecule (see Table 6).

Three N–N bridges of three thiadiazole rings of distinct L^4 ligands link adjacent Ag^I centre [Ag(1) and Ag(2)] with the Ag \cdots Ag distance of 3.44(3) Å, forming three six-membered rings, all adopting a chair conformation. Two such polycyclic ring units are connected through the alkyl linker units of two L^4 ligands, forming the tetranuclear macrometallocycle as shown in Fig. 5a. There is an inversion centre at the midpoint of the C(4)–C(4A) bond and the one-dimensional chain is propagated by further inversion related movements as shown in Fig. 5b.

The replacement of the strongly coordinating NO_3^- anions by the more weakly coordinating ClO_4^- anions has a profound effect upon the network formation. The perchlorate anions are located up and down the tetranuclear plane, and the weak interaction of the O atom of perchlorate anion with the S atoms of the linker chain of L^4 ligand (S \cdots O distance being 3.13(4), 3.25(3) and 3.29(3) Å, respectively) may prevent the S atom from the coordination with the metal centre, resulting in that only N donors of L^4 ligand coordinate to the Ag^I atoms.

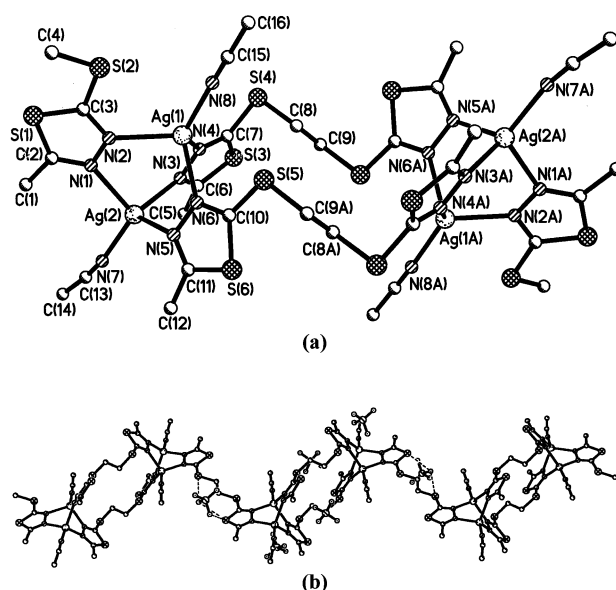


Fig. 5 (a) The tetranuclear unit and (b) the 1D structure of **5** (symmetry codes: $1-x, 1-y, 1-z$).

Conclusions

Five different Ag^I coordination complexes (**1–5**) with four nitrogen-containing heterocyclic dithioether ligands (L^1 – L^4) have been prepared and structurally characterized, giving metal–organic supramolecular architectures from dinuclear to three-dimensional structures. Ag^I centres adopt three- or four-coordination modes with different coordination environments. The chain length of the linker unit affects the coordination mode of the terminal group greatly: The four-membered rings that would be formed by the two S donors in L^1 (or L^3) coordinating to the Ag^I centre are more geometrically strained than the corresponding five-membered rings that would be formed in L^2 (or L^4), and hence less favoured. Otherwise, two carbons in the linker unit of L^2 and L^4 results in more flexibility and variety of the coordination modes of the terminal groups and the complexity of the structures. Also, it should be noted that although Ag is a ‘soft’ metal, it prefers to coordinate to an N atom first rather than an S atom, despite the fact that S is a more ‘soft’ base. This indicates that geometrical effects may play more important roles than the electronic effects in controlling the formation of these structures. In addition, the structure of the terminal group and the environment of the donors also greatly influence the structure construction, as well as the counter anions. In conclusion, the terminal group and the chain length of the linker unit greatly influence the coordination modes of the metal centres, indicating that the nature of the ligand is a determining factor in controlling the structural topology of these metal–organic supramolecular architectures, and this offers the opportunity in controlling the coordination networks by ligand modifications.

Experimental

Materials and general methods

All the reagents required for syntheses were obtained commercially and purified by standard methods prior to use. Melting points were measured on a X-4 micro melting point detector without further correction. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. IR spectra were measured on a 170SX (Nicolet) FT-IR spectrometer with KBr pellets. 1H NMR spectra were recorded on a Bruker AC-P300 spectrometer (300 MHz) at 25 °C in $CDCl_3$ for the ligands and in CD_3CN for the Ag^I complexes with tetramethylsilane as the

internal reference. Thermal stability (TG-DTA) studies were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 610 °C for complexes 1–4 and to 200 °C for complex 5.

Syntheses of ligands

2,2'-[Methylenebis(thio)]bis(pyrimidine) (L¹). According to the reported procedure,¹⁶ 2-mercaptopyrimidine (1.12 g, 10 mmol) was added to a stirred solution of KOH (0.56 g, 10 mmol) in ethanol (20 mL). The mixture was warmed to refluxed, then 1,1-dibromomethane (0.87 g, 5 mmol) was added dropwise and the mixture was refluxed for about 6 h. After adding additional water (30 mL), the mixture was left to stand overnight. The precipitate was filtered off and washed with ethanol and water, giving a fine white powder in 85% yield, mp 155–157 °C. Anal. Calc. for C₉H₈N₄S₂, C, 45.76; H, 3.39; N, 23.73. Found: C, 45.65; H, 3.43; N, 23.58. ¹H NMR (300 MHz, CDCl₃), δ 8.57 (d, 4H, C=CH–N), 7.02 (t, 2H, CH=C–N), 4.94 (s, 2H, S–CH₂–S).

2,2'-[1,2-Ethanedylbis(thio)]bis(pyrimidine) (L²). Reaction of 2-mercaptopyrimidine (1.12 g, 10 mmol) with 1,2-dibromoethane (0.94 g, 5 mmol) as described above for L¹,¹⁶ giving compound L² as a white powder in 50% yield, mp 157–159 °C. Anal. Calc. for C₁₀H₁₀N₄S₂, C, 48.00; H, 4.00; N, 22.40. Found: C, 47.88; H, 4.06; N, 22.24. ¹H NMR (300 MHz, CDCl₃), δ 8.53 (d, 4H, C=CH–N), 6.99 (t, 2H, CH=C–N), 3.53 (s, 4H, S–CH₂).

2,2'-[Methylenebis(thio)]bis[5-methyl-1,3,4-thiadiazole] (L³). Reaction of 5-methyl-2-sulfanyl-1,3,4-thiadiazole (1.32 g, 10 mmol) with 1,1-dibromomethane (0.87 g, 5 mmol) as described above for L¹, giving compound L³ as a white powder in 84% yield, mp 78–80 °C. Anal. Calc. for C₇H₈N₄S₂, C, 30.43; H, 2.90; N, 20.29. Found: C, 30.13; H, 2.78; N, 19.67. ¹H NMR (300 MHz, CDCl₃), δ 5.19 (s, 2H, S–CH₂–S), 2.76 (s, 6H, CH₃).

2,2'-[1,2-Ethanedylbis(thio)]bis(5-methyl-1,3,4-thiadiazole) (L⁴). Reaction of 5-methyl-2-sulfanyl-1,3,4-thiadiazole (1.32 g, 10 mmol) with 1,2-dibromoethane (0.94 g, 5 mmol) as described above for L¹,¹⁶ giving compound L⁴ as a white powder in 87% yield, mp 135–136 °C. Anal. Calc. for C₈H₁₀N₄S₂, C, 33.10; H, 3.45; N, 19.31. Found: C, 32.97; H, 3.42; N, 19.18. ¹H NMR (300 MHz, CDCl₃), δ 3.76 (s, 4H, S–CH₂), 2.74 (s, 6H, CH₃).

Syntheses of the complexes 1–5. Colorless single crystals suitable for X-ray analyses for all complexes were obtained by the similar method as described below.

[AgL¹NO₃]₂, 1. A solution of AgNO₃ (179 mg, 1 mmol) in acetonitrile (30 mL) was added to the solution of L¹ (236 mg, 1 mmol) in chloroform (30 mL). The reaction mixture was stirred for 10 min to give a colorless solution, and then filtered. Slow diffusion of acetone into the resulting solution yielded colorless single crystals in 60% yield. Anal. Calc. for C₉H₈AgN₅O₃S₂: C, 26.59; H, 1.97; N, 17.23. Found: C, 25.94; H, 2.06; N, 17.10. IR (KBr pellet, cm⁻¹): 3121w, 2935w, 1634w, 1560s, 1551s, 1383vs, 1312s, 1262m, 1172s, 1035m, 832m, 766s, 756m, 640m. ¹H NMR (300 MHz, CD₃CN), δ 8.59 (d, 4H, C=CH–N), 7.16 (t, 2H, CH=C–N), 4.90 (s, 2H, S–CH₂–S). DTA data (peak position): 190 and 262 °C.

[AgL²NO₃]₂, 2. Yield: 58%. Anal. Calc. for C₂₀H₂₀Ag₂N₁₀O₆S₄: C, 28.56; H, 2.38; N, 16.66. Found: C, 28.88; H, 2.38; N, 16.98. IR (KBr pellet, cm⁻¹): 3110w, 2985w, 1637w, 1561s, 1549s, 1379vs, 1304s, 1247m, 1183s, 1032m, 811m, 766m, 749m, 641m. ¹H NMR (300 MHz, CD₃CN), δ 8.56 (d, 4H, C=CH–N), 7.12 (t, 2H, CH=C–N), 3.51 (s, 4H, S–CH₂). DTA data (peak position): 196 and 279 °C.

[AgL³(NO₃)(H₂O)]₂, 3. Yield: 64%. Anal. Calc. for C₇H₁₀AgN₅O₄S₄: C, 18.09; H, 2.15; N, 15.08. Found: C, 17.83; H, 2.29; N, 15.33. IR (KBr pellet, cm⁻¹): 3442s, 2972m, 2918m, 1635m, 1487m, 1384vs, 1229m, 1189s, 1165m, 1071s, 1038s, 826s, 715s, 615s. ¹H NMR (300 MHz, CD₃CN), δ 5.07 (s, 2H, S–CH₂–S), 2.70 (s, 6H, CH₃). DTA data (peak position): 64, 119 and 224 °C.

[Ag₂L⁴(NO₃)₂]₂, 4. Yield: 65%. Anal. Calc. for C₈H₁₀Ag₂N₆O₆S₄: C, 15.23; H, 1.59; N, 13.33. Found: C, 15.17; H, 1.59; N, 13.23. IR (KBr pellet, cm⁻¹): 2925w, 2852w, 1762m, 1628w, 1488m, 1385vs, 1213s, 1194s, 1141m, 1068vs, 1032s, 825s, 729s, 617s. ¹H NMR (300 MHz, CD₃CN), δ 3.65 (s, 2H, S–CH₂), 2.68 (s, 3H, CH₃). DTA data (peak position): 187 and 250 °C.

[Ag₂L⁴(CH₃CN)₂](ClO₄)₂]₂, 5. Yield: 54%. Anal. Calc. for C₁₆H₂₁Ag₂Cl₂N₈O₈S₆: C, 20.59; H, 2.25; N, 12.01. Found: C, 20.33; H, 2.38; N, 12.38. IR (KBr pellet, cm⁻¹): 2993w, 2926w, 2720w, 2170w, 1627m, 1486m, 1429m, 1407s, 1376s, 1212s, 1194s, 1141s, 1107vs, 1089vs, 1068vs, 1032s, 760m, 730m, 625s. ¹H NMR (300 MHz, CD₃CN), δ 3.64 (s, 6H, S–CH₂), 2.69 (s, 9H, CH₃), 1.97 (s, 6H, CH₃CN). DTA data (peak position): 149 and 184 °C.

Caution! Although we have met no problems in handling perchlorate salts during this work, these should be treated with great caution owing to their potentially explosive nature.

X-Ray crystallography

Single-crystal X-ray diffraction measurements for complexes 1–5 were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. The determinations of unit cell parameters and data collections were performed with Mo-K α radiation ($\lambda = 0.71073$ Å) and unit cell dimensions were obtained with least-squares refinements. The program SAINT¹⁷ was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL.¹⁸ All the non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 . The hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factors.

CCDC reference numbers 200123–200127.

See <http://www.rsc.org/suppdata/dt/b2/b212499h/> for crystallographic data in CIF or other electronic format.

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