FULL PAPER

Novel dithioether–silver(I) coordination architectures: structural diversities by varying the spacers and terminal groups of ligands[†]

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An investigation into the dependence of the framework formation of coordination architectures on ligand spacers and terminal groups was reported based on the self-assembly of AgClO₄ and eight structurally related flexible dithioether ligands, RS(CH₂)_nSR (L_a^n , R = ethyl group; L_b^n , R = benzyl group, n = 1-4). Eight novel metal–organic architectures, $[Ag(L_a^1)_{3/2}ClO_4]_n$ (1a), $[Ag_2(L_a^2)_2(ClO_4)_2]_2$ (2a), $[AgL_a^3ClO_4]_n$ (3a), $\{[Ag(L_a^4)_2]ClO_4\}_n$ (4a), $[AgL_b^1ClO_4]_2$ (1b), $[Ag(L_b^{4})_2]ClO_4$ (2b), $\{[Ag(L_b^{3})_{3/2}(ClO_4)_{1/2}](ClO_4)_{1/2}\}_n$ (3b) and $[Ag(L_b^{4})_{3/2}ClO_4]_n$ (4b), were synthesized and structurally characterized by X-ray crystallography. Structure diversities were observed for these complexes: 1a forms a 2-D (6,3) net, while 2a is a discrete tetranuclear complex, in which the Ag¹ ion adopts linear and tetrahedral coordination modes, and the S donors in each ligand show monodentate terminal and μ_2 -S bridging coordination fashions; 3a has a chiral helical chain structure in which two homo-chiral right-handed single helical chains $(Ag-L_a^3-)_n$ are bound together through μ_2 -S donors, and simultaneously gives rise to left-handed helical entity $(Ag-S-)_n$. In 4a, left- and right-handed helical chains formed by the ligands bridging Ag¹ centers are further linked alternately by single-bridging ligands to form a non-chiral 2-D framework. 1b has a dinuclear structure showing obvious ligand-sustained Ag–Ag interaction, while 2b is a mononuclear complex; 3b is a 3-D framework formed by ClO_4^{-} linking the 2-D (6,3) framework, which is similar to that of 1a, and 4b has a single, double-bridging chain structure in which 14-membered dinuclear ring units formed through two ligands bridging two Ag¹ ions are further linked by single-bridging ligands. In addition, a systematic structural comparison of these complexes and other reported AgClO₄ complexes of analogous dithioether ligands indicates that the ligand spacers and terminal groups take essential roles on the framework formation of the Ag¹ complexes, and this present feasible ways for adjusting the structures of such complexes by modifying the ligand spacers and terminal groups.

Introduction

In recent years, the construction of metal-organic coordination architectures has continued to attract great attention due to not only the intriguing variety of their structures and new topologies, but also their potential applications as new materials.¹⁻³ Considerable efforts have been made on the theoretical predication and network-based approaches for controlling the topology and geometries of the networks to produce useful functional materials,^{4,5} and some successes have been reported, however, no method gave consistently reliable predictions, as stated by Dunitz,⁶ because the self-assembly progress is highly affected by several factors such as the nature of the ligand,⁷ solvents,⁸ templates (or guests),⁹ and counterions,¹⁰ and so on. Therefore, to understand the fine-drawn connection between complex structures and the factors that affecting the framework formation is still one of the key points for the rational design of crystalline materials, and still seems to be a great challenge.

Although rigid pillar organic units are usually employed as bridging ligands to build extended networks with metal ions,¹¹ recently, there is an increasing interest to coordination architectures using flexible bridging ligands,¹² and various coordination architectures with diverse structures and different types of flexible bridging ligands have been reported, particularly, those containing N- or O-donors, for example, bis(4-pyridyl).¹²⁷ Such studies have shown that the nature of the anions, terminal groups and the spacer length of these bridging ligands play fundamental roles in determining the structural types of the final assemblies. However, systematic investigations on the dependence of such factors with the framework formations of complexes are sill comparatively rare.

† Electronic supplementary information (ESI) available: Experimental and calculated powder diffraction patterns. See http://www.rsc.org/ suppdata/dt/b4/b416576b/

Ag^I is a favorable and fashionable building block or connecting node for constructing coordination architectures due to its coordination diversity and flexibility.13 Therefore, the investigations of Ag^I complexes with flexible ligands are of significance for investigating the relationship between the complex structures and ligands nature, solvent, counter anions and other factors. In order to obtain information at the basic structural level, of interest for the crystal engineering of novel coordination architectures, our recent efforts12i-o have focused on the investigation of the framework formations of flexible dithioether ligands (as depicted in Chart 1) with Ag^I salts. Herein, we report a systematic study of the self-assembly of eight structurally related flexible dithioether ligands $RS(CH_2)_{\mu}SR$ (R = ethyl or benzyl group, n = 1-4) with AgClO₄. Combining other reported Ag^I complexes with related ligands, the relationships among complex structures and the spacer length and terminal groups of such ligands were also discussed.

Experimental

General

All the reagents for synthesis were commercially available and used as received. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. IR spectra (KBr pellets) were taken on a FT-IR 170SX (Nicolet) spectrometer. ¹H NMR spectra were measured on a Bruker AC-P500 spectrometer (300 MHz) at 25 °C with tetramethylsilane as the internal reference. The dithioether ligands: bis(ethylthio)methane (L_a^1), 1,2bis(ethylthio)ethane (L_a^2), 1,3-bis(ethylthio)propane (L_a^3), 1,4bis(ethylthio)butane (L_a^4), bis(benzylthio)methane (L_b^1), 1,2bis(benzylthio)ethane (L_b^2), 1,3-bis(benzylthio)propane (L_b^3) and 1,4-bis(benzylthio)butane (L_b^4) were synthesized by the reaction of homologous bis(bromo)alkane with potassium



Chart 1 Some flexible dithioether ligands involved in this paper.

ethylthiolate (or benzylthiolate) according to the similar literature method.¹⁴ ¹H NMR (CDCl₃) for L_a¹: δ 3.70 (s, 2H, S– CH₂–S), 2.66 (q, 4H, MeCH₂–S), 1.27 (t, 6H, Me); L_a²: δ 2.74 (s, 4H, CH₂–S), 2.57 (q, 4H, MeCH₂–S), 1.27 (t, 6H, Me); L_a³: δ 2.63 (t, 4H, CH₂–S), 2.55 (q, 4H, MeCH₂–S), 1.88 (t, 2H, CH₂CH₂–S), 1.26 (t, 6H, Me); L_a⁴: δ 2.57 (t, 4H, CH₂–S), 2.53 (q, 4H, MeCH₂–S), 1.68 (t, 4H, CH₂CH₂–S), 1.26 (t, 6H, Me); L_b¹: δ 7.22–7.31 (m, 10H, Ph), 3.84 (s, 4H, S–CH₂–Ph), 3.37 (s, 2H, S–CH₂–S); for L_b²: δ 7.22–7.34 (m, 10H, Ph), 3.68 (s, 4H, S–CH₂–Ph), 2.56 (s, 4H, CH₂–S); L_b³: δ 7.21–7.33 (m, 10H, Ph), 3.66 (s, 4H, S–CH₂–Ph), 2.46 (t, 4H, CH₂–S), 1.80 (t, 2H, CH₂CH₂–S); L_b⁴: δ 7.22–7.32 (m, 10H, Ph), 3.68 (s, 4H, S–CH₂– Ph), 2.37 (t, 4H, CH₂–S), 1.61 (t, 4H, CH₂CH₂–S).

Syntheses of complexes

Colorless single crystals suitable for X-ray analyses for all complexes were obtained by the similar method as described below: to a solution of $AgClO_4$ ·H₂O (0.3 mmol) in acetone (6 mL) was slowly added a chloroform solution (6 mL) of ligand (0.6 mmol). The mixture was stirred for about 10 min and filtered. Crystals were obtained by slow diffusion of ether to above filtrate in the dark. All general characterizations are carried out based upon the crystal samples.

 $[Ag(L_a^{-1})_{3/2}ClO_4]_n$ 1a. Yield: 71%. Anal. Calc. for $C_{7.5}H_{18}S_3$ -AgClO₄: C, 21.88; H, 4.41. Found: C, 21.41; H, 4.06%. IR (KBr pellet, cm⁻¹): 2967m, 2019w, 1633w, 1456m, 1382m, 1212m, 1097s, 838w, 782w, 729m, 624s.

 $[Ag_2(L_a^2)_2(CIO_4)_2]_2$ 2a. Yield: 78%. Anal. Calc. for $C_{12}H_{28}S_4$ -Ag_2 Cl_2O_8 : C, 20.15; H, 3.95. Found: C, 19.97; H, 3.62%. IR (KBr pellet, cm⁻¹): 2966m, 2019w, 1624w, 1451w, 1376w, 1257w, 1094s, 941w, 716w, 628s.

 $[AgL_a^3CIO_4]_n$ 3a. Yield: 75%. Anal. Calc. for $C_7H_{16}S_2$ -AgClO₄: C, 22.62; H, 4.34. Found: C, 22.38; H, 4.09%. IR (KBr pellet, cm⁻¹): 2964m, 2921m, 2017w, 1636w, 1450m, 1375w, 1254w, 1142s, 1094s, 839w, 783w, 628s.

 $\{[Ag(L_a^4)_2]CIO_4\}_n$ 4a. Yield: 69%. Anal. Calc. for $C_{16}H_{36}S_4$ -AgCIO₄: C, 34.07; H, 6.43. Found: C, 33.91; H, 6.14%. IR (KBr pellet, cm⁻¹): 2971m, 2020w, 1631w, 1457m, 1370m, 1251w, 1106s, 1093s, 724w, 621m.

[AgL_b¹ClO₄]₂ 1b. Yield: 81%. Anal. Calc. for $C_{15}H_{16}S_{2}$ -AgClO₄: C, 38.52; H, 3.45. Found: C, 38.31; H, 3.12%. IR (KBr pellet, cm⁻¹): 3027w, 2915w, 1628w, 1493m, 1453m, 1417w, 1242w, 1095s, 915w, 769w, 699m, 628m, 564w, 471w.

 $[Ag(L_b^2)_2]CIO_4$ 2b. Yield: 69%. Anal. Calc. for $C_{32}H_{36}S_4$ -AgCIO₄: C, 50.83; H, 4.80. Found: C, 50.61; H, 4.54%. IR (KBr pellet, cm⁻¹): 3027w, 2915w, 1601w, 1494m, 1453m, 1421w, 1241w, 1094s, 941w, 768w, 698m, 627m, 564w, 472w.

{ $[Ag(L_b^3)_{3/2}(ClO_4)_{1/2}](ClO_4)_{1/2}]_n$ 3b. Yield: 69%. Anal. Calc. for C_{25.5}H₃₀S₃AgClO₄: C, 47.86; H, 4.72. Found: C, 47.61; H, 4.24%. IR (KBr pellet, cm⁻¹): 3021, 2960w, 1637w, 1494m, 1453m, 1359s, 1200s, 1071s, 784m, 714s, 700s, 562w.

 $[Ag(L_b^4)_{3/2}ClO_4]_n$ 4b. Yield: 59%. Anal. Calc. for $C_{27}H_{33}S_3$ -AgClO₄: C, 49.06; H, 5.03. Found: C, 48.96; H, 4.94%. IR (KBr pellet, cm⁻¹): 3018, 2918m, 1630w, 1494m, 1453m, 1282w, 1144s, 1092s, 769w, 700m, 628s, 566w.

CAUTION. Although we experienced no problems in this work, perchlorate salts of metal complexes with organic ligands are often explosive and should be handled with great caution.

X-Ray structure determination

Single-crystal X-ray diffraction measurements for all the complexes were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator at 298(2) K. The determination of unit cell parameters and data collections were performed with Mo-K α radiation (λ = 0.71073 Å). Unit cell dimensions were obtained with leastsquares refinements. The program SAINT¹⁵ was used for integration of the diffraction profiles. All the structures were solved by direct methods combining successive difference Fourier syntheses using the SHELXS program of the SHELXTL package and refined with SHELXL.¹⁶ 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, and riding on the concerned atoms and refined with fixed thermal factors. The disorders of the ligands or perchlorate were found in some complexes, and a suitable site occupation separation was used for refinement in each case. Especially, in 4a, there is imposed symmetry at the disordered C12 and C16 sites, and the disordered atoms (C12 and C12'; C16 and C16') are related by an inversion center in each case. For C16, the refinement gives a cyclohexane-like ring. In 3b, perchlorate ions are highly disordered and lie on high symmetry sites. Although the relevant modes have been developed, attempts for obtaining a perfect data are unsuccessful. In this text part of disordered atoms/groups were omitted in drawing figures. Crystallographic data and experimental details for structural analyses are summarized in Table 1 and the selected bond lengths and angles are listed in Table 2.

CCDC reference numbers 231504–231511.

See http://www.rsc.org/suppdata/dt/b4/b416576b/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and general characterization

All the complexes were obtained by the self-assembly of AgClO₄ with bis(ethylthio)alkane (L_a^n) or bis(benzylthio)alkane (L_b^n) ligand in the similar reaction conditions. Although the same ratio of Ag/L (1:2) was used in the procedures for synthesizing all these complexes, that in the resulted products was found to be different (1 : 1, 2 : 3 or 1 : 2). The elemental analyses showed that the components of these complexes are consistent with the results of crystal structures. The syntheses were repeated for all the eight compounds with the reaction stoichiometric ratio of the corresponding crystal structure, respectively, in order to confirm if the resulted materials in such situation are the same as the corresponding single crystals. The polycrystalline compound was obtained by adding ether directly to the reaction system. X-Ray powder diffraction results show that only 1a, 3a and 3b have the same diffraction patterns (see ESI[†]) to those simulated by the crystal data of the corresponding complex. This

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 Table 1
 Crystallographic data and structural refinement details for complexes 1a-4b

	1a	2a	За	4a	1b	2b	3b	4b
Formula	$C_{15}H_{36}S_6Ag_2Cl_2O_8$	C ₂₄ H ₅₆ S ₈ Ag ₄ Cl ₄ O ₁₆	$C_7H_{16}S_2AgClO_4$	$\mathrm{C}_{16}\mathrm{H}_{36}\mathrm{S}_4\mathrm{AgClO}_4$	$\mathrm{C_{15}H_{16}S_{2}AgClO_{4}}$	$C_{32}H_{36}S_4AgClO_4$	$C_{51}H_{60}S_6Ag_2Cl_2O_8$	C ₂₇ H ₃₃ S ₃ AgClO ₄
M _r Crvstal svstem	823.44 Trigonal	1430.45 Monoclinic	3/1.64 Orthorhombic	564.01 Monoclinic	467.72 Monoclinic	/26.1/ Monoclinic	Trioonal	661.03 Monoclinic
Space group	$P\bar{3}c1$	$P2_1/c$	$P2_{1}2_{1}2_{1}$	$P2_1/c$	C2/c	$P2_1/c$	$R\bar{3}c$	$P2_1/n$
a/Å	10.881(3)	12.628(4)	7.506(2)	13.535(15)	35.61(1)	14.908(6)	15.625(3)	9.604(5)
$b/\text{\AA}$	10.881(3)	12.126(4)	11.300(4)	9.765(10)	6.244(2)	18.868(7)	15.625(3)	23.66(1)
c/Å	15.660(8)	16.977(5)	15.348(5)	19.45(2)	17.561(6)	13.658(5)	39.55(1)	12.399(6)
$a/^{\circ}$	60	90	90	90	90	90	06	60
$\beta/^{\circ}$	90	109.443(6)	90	102.014(19)	114.498(6)	116.710(6)	90	96.660(9)
y /0	120	90	90	06	06	90	120	90
$V/Å^3$	1606(1)	2452(1)	1301.8(7)	2514(5)	3552(2)	3432(2)	8362(4)	2798(2)
$D_{ m c}/{ m Mg}~{ m m}^{-3}$	1.703	1.938	1.896	1.490	1.749	1.464	1.525	1.569
Z	7	0	4	4	8	4	6	4
μ/mm^{-1}	1.809	2.190	2.066	1.257	1.535	0.943	1.073	1.072
Refl. collected	4145	11377	6077	10268	6066	19635	11372	15215
Unique refl. (R_{int})	934 (0.0589)	4874 (0.0652)	2592 (0.0436)	4325 (0.0960)	3639~(0.0633)	7061 (0.0399)	1713(0.0449)	5742 (0.0891)
Goodness of fit	1.014	0.951	1.013	0.999	1.000	1.064	1.035	0.952
$R1^{a} [I > 2\sigma(I)]$	0.0355	0.0462	0.0495	0.0669	0.0462	0.0492	0.0434	0.0585
$wR2^{b}$ (all data)	0.0962	0.0824	0.1135	0.1674	0.1252	0.1406	0.1230	0.1351

1a			
Ag(1)–S(1) Ag(1)–O(1)	2.509(1) 2.589(7)	S(1)-Ag(1)-S(1A) S(1)-Ag(1)-O(1)	117.84(2) 98.52(3)
2a			
Ag(1)-S(1) Ag(1)-S(4A) Ag(2)-S(1) Ag(2)-S(2) Ag(2)-S(3) Ag(2)-S(4) Ag(1)-O(1) Ag(1)-O(6A)	2.464(2) 2.447(2) 2.632(2) 2.545(2) 2.520(2) 2.651(2) 2.648(5) 2.67(2)	$\begin{array}{c} S(1)-Ag(1)-S(4A)\\ S(1)-Ag(2)-S(2)\\ S(1)-Ag(2)-S(3)\\ S(1)-Ag(2)-S(3)\\ S(2)-Ag(2)-S(4)\\ S(2)-Ag(2)-S(4)\\ S(3)-Ag(2)-S(4)\\ S(3)-Ag(2)-S(4)\\ Ag(1)-S(1)-Ag(2)\\ Ag(2)-S(4)-Ag(1A)\\ \end{array}$	162.36(5) 82.54(5) 124.47(5) 115.12(5) 145.02(6) 106.22(5) 83.43(5) 125.48(6) 121.10(6)
3a			
Ag(1)–S(1) Ag(1)–S(1B) Ag(1)–S(2A) Ag(1)–O(3)	2.544(2) 2.565(2) 2.504(2) 2.53(2)	$\begin{array}{l} S(1)-Ag(1)-S(2A)\\ S(1)-Ag(1)-S(1B)\\ S(1)-Ag(1)-O(3)\\ S(2A)-Ag(1)-S(1B)\\ O(3)-Ag(1)-S(2A)\\ O(3)-Ag(1)-S(2A)\\ O(3)-Ag(1)-S(1B)\\ Ag(1)-S(1)-Ag(1C) \end{array}$	125.85(8) 122.04(5) 99.6(4) 111.40(8) 92.7(7) 85.0(6) 120.20(8)
4a			
Ag(1)–S(1) Ag(1)–S(3) Ag(1)–S(4) Ag(1)–S(2A)	2.598(3) 2.607(3) 2.553(3) 2.609(3)	$\begin{array}{c} S(1)-Ag(1)-S(3)\\ S(1)-Ag(1)-S(4)\\ S(1)-Ag(1)-S(2A)\\ S(3)-Ag(1)-S(4)\\ S(3)-Ag(1)-S(4)\\ S(3)-Ag(1)-S(2A)\\ S(4)-Ag(1)-S(2A) \end{array}$	105.7(1) 107.78(9) 113.0(1) 116.4(1) 100.6(1) 113.21(9)
1b			
	2.442(2) 2.445(2) 3.036(1) 2.639(5) 2.639(6)	S(1)-Ag(1)-S(2)	166.65(5)
Ag(1)–S(1)	2.604(1)	S(1)-Ag(1)-S(2)	85.17(5)
Ag(1)–S(2) Ag(1)–S(3) Ag(1)–S(4)	2.515(1) 2.523(1) 2.590(1)	$\begin{array}{l} S(1)-Ag(1)-S(3)\\ S(1)-Ag(1)-S(4)\\ S(2)-Ag(1)-S(3)\\ S(2)-Ag(1)-S(4)\\ S(3)-Ag(1)-S(4)\\ \end{array}$	110.93(4) 120.14(4) 141.27(4) 116.36(5) 86.58(5)
3b			
Ag(1)–S(1) Ag(1)–O(1)	2.502(1) 2.22(1)	S(1)-Ag(1)-S(1A)	119.766(5)
4b			
$ \begin{array}{r} Ag(1)-S(1) \\ Ag(1)-S(2) \\ Ag(1)-S(3) \\ Ag(1)-O(1) \\ \end{array} $	2.509(2) 2.524(2) 2.512(2) 2.723(6)	S(1)-Ag(1)-S(2) S(1)-Ag(1)-S(3) S(2)-Ag(1)-S(3)	110.82(6) 124.19(6) 122.56(5)

Table 2 Selected bond lengths (Å) and angles (°) for complexes 1a–4b

A: 2 - x, y + 1/2, 1/2 - z. **1b**, A: 1 - x, 1 - y, 1 - z; B: x, y - 1, z. **3b**, A: 2 - y, x - y + 1, z. result shows that maybe the 1 : 2 ratio is suitable for obtaining the corresponding crystals, but that the correct stoichiometry

may lead to the formation of other compounds. It should be noted that some of these Ag^I complexes are not stable in light. The difference between the diffraction patterns of the powder samples and the crystal data of the same complex may also be attributed to this instability.

IR spectra of the complexes are similar and show the characteristic S-C vibrations at about 700 cm⁻¹ and the existence

Description of crystal structures

 $[Ag(L_a^1)_{3/2}ClO_4]_n$ 1a, a 2-D (6,3) net. 1a has a 2-D layer structure of (6,3) topology, with the Ag^I ions, related by a three-fold axis equally coordinated to three S donors from three distinct L_a^1 , and an O atom of disordered ClO_4^- (Fig. 1(a)) The coordination geometry of AgI center can be described as a regular triangle pyramid with three S donors lying in the equatorial plane and one O atom in the apical position. The Ag-S and Ag-O bond lengths are 2.509(1) and 2.589(7) Å, respectively, and the S-Ag-S angle is 117.84(2)°. The Ag^I ion deviates from the S_3 plane by 0.372(1) Å due to the axial coordination of ClO_4^- . As shown in Fig. 1(b), in **1a** each ligand links two Ag^I through the S atoms and each Ag^I is bridged to three neighboring Ag^{I} ions by L_{a}^{1} to form centrosymmetric hexagonal 24-membered $(AgL_a^{1})_6$ macrometallacyclic units (Fig. 1(c)), in which six Ag^I atoms are located alternately up and down. The central C atom (C3) of each ligand lies on a twofold axis. In the macrometallacyclic unit the distance of adjacent Ag^I ions is 6.475(2) Å and the S····S distance in L_a^{-1} is 3.012(3) Å. Eventually, the macrometallacyclic unit extends out along a and b directions to form a 2-D (6,3) layer (Fig. 1(c)). In addition, three ethyl groups of the $\mathbf{L}_a{}^1$ ligand and $\text{ClO}_4{}^-$ around each Ag^I are located at the same side of the layer and those around adjacent Ag^I are at the opposite sides, which may help to reduce the steric hindrance. The two S atoms of each ligand show R,S (or S, R) configuration, but three around each Ag^I center are the same S or R configuration.

Another particular feature of 1a is that the 2-D layers stack in an ABAB alternating fashion with 30° turning around the threefold axis through Ag^I centers, but without offsetting each other, and ClO₄⁻ is located between these layers (Fig. 1(d)). Due to the highly disorder of ClO_4^- , the weak coordination interactions between O atoms in one layer and Ag¹ ions from adjacent layers can not be established, however, they can be regarded as pillars to sustain such layers. Thus, this type of layer packing gives rise to a quasi-3-D framework and shows brick-wall structure in the direction paralleling such layers. Space-filling views of the structure reveal small channels that run parallel to the *z* axis. Calculations from the X-ray structural parameters show that the solvent-accessible void space in the channels is approximately 6.5%.¹⁷ The smallest diameter of these channels, after taking into account the van der Waals radii, is *ca.* 2.3 Å.

 $[Ag_2(L_a^2)_2(ClO_4)_2]_2$ 2a, a tetranuclear complex. 2a is a tetranuclear molecule, consisting of tetranuclear $[Ag_2(L_a^2)_2]_2$ cations and ClO₄⁻ anions which weakly coordinate to Ag^I ions (Fig. 2(a)), and the cation has a "hexagonal" tetranuclear macrometallacyclic geometry with the crystallographic inversion center located at the center of the molecule, and consists of four Ag^{I} and four L_{a}^{2} ligands. In the macrometallacycle, two pairs of Ag^I ions adopt different coordination modes and environments. Ag1 is coordinated to two S donors from two L_a² in quasi-linear geometry with the S-Ag-S angle being 162.36(5)°, which deviates from 180° due to the weak coordination of ClO_4 (vide infra), and the Ag1-S1 and Ag1-S4A bond distances are 2.464(2) and 2.447(2) Å, respectively. While Ag2 has a highly distorted tetrahedral coordination geometry formed by four S donors from two chelating L_a^2 ligands, and the Ag2–S bond distances lie between 2.520(2) and 2.651(2) Å which are longer than those of Ag1-S, but being normal for Ag^I complexes of thioether ligands,¹⁸ and the bond angles around Ag2 center range from 82.54(5) to 145.02(6)°.

In **2a** each ligand takes chelating and bridging coordination roles, with the S donors exhibiting monodentate terminal and μ_2 -bridging coordination modes. As shown in Fig. 2(a), in the cation unit, a pair of ligands coordinate to Ag2 atom in chelating mode using its two S donors to form two five-membered rings and simultaneously bridge Ag1 and Ag1A ions through one of





Fig. 1 (a) View of the coordination environment of Ag¹ in 1a, (b) the ligand linking mode in 1a, (c) the 2-D (6,3) layer structure of 1a (the ethyl groups were omitted for clarity) and (d) quasi-3-D framework perspective viewing along *z*-axis showing channels. Symmetry codes, A: 1 - y, x - y + 1, *z*; B: y - x, 1 - x, *z*; C: x - y + 1, 2 - y, 1/2 - z.





Fig. 2 (a) View of the tetranuclear structure of **2a** and (b) 2-D (4,4) network along the *bc* plane in **2a** formed through ClO_4^- linking the tetranuclear cations (the ethyl groups are omitted for clarity in (b)). Symmetry code, A: 1 - x, 1 - y, 1 - z.

the S donors of each ligand in μ_2 -S bridging coordination mode. Similarly, the other pair of ligands coordinate to Ag2A and bridge Ag1 and Ag1A ions. The chelating and bridging coordination give rise to a tetranuclear Ag₄S₄ ring entity, in which four Ag atoms and four S atoms are coplanar, respectively, and the dihedral angle between them is 10.69(5)°. The intramolecular Ag...Ag separations are 4.531(1) Å for Ag1...Ag2, 4.441(1) Å for Ag1...Ag2A, 4.768(2) Å for Ag1...Ag1A and 7.600(2) Å for Ag2...Ag2A, respectively. The S atoms of each L_a² ligand around Ag2 (or Ag2A) show *R*,*S* (or *S*,*R*) configuration, and those around Ag1 (or Ag1A) are also *R*,*S* (or *S*,*R*). This type of structure, and the coordination modes of the ligand in 1a are unique for Ag¹ complexes with bithioethers.

It is interesting that these tetranuclear cations are further linked through weak coordination of $Ag \cdots O$ by disordered ClO_4^- to form a 2-D sheet (Fig. 2(b)). In each $[Ag_2(L_a^2)_2]_2$ molecule, two ClO_4^- anions weakly coordinate to Ag1 and Ag1A ions in the periphery with the Ag1–O1 (Ag1A–O1A) and Ag1–O2 (Ag1A–O2A) distances of 2.648(5) and 3.080(6) Å, respectively. The other two also weakly coordinate to Ag1 and Ag1A ions with Ag1–O5 = 2.93(2), Ag1–O6A = 2.67(2) and Ag1A–O6' = 2.68(1) Å in O–Cl–O bridging fashion to form an eight-membered (–Ag–O–Cl–O)₂ ring, then the other O atoms (O7 and O7A) in the two ClO_4^- anions further link the Ag2 and Ag2A ions of adjacent Ag₄S₄ units (Ag2–O7B = 3.044(9)Å, symmetry code B: 1 - x, 1/2 + y, 1/2 - z) to form a 2-D network along the *bc* plane. If the Ag₄S₄ entity could be regarded as a "node" and the ClO₄⁻ as a "spacer", the 2-D network can be described as a (4,4) topology.

 $[AgL_a^{3}ClO_4]_n$ 3a, a chiral helical chain. 3a is a chiral helical chain polymer consisting of $(AgL_a^{3}ClO_4)$ units (Fig. 3(a)), in



Fig. 3 (a) View of the coordination environment of Ag^{1} in **3a**, (b) side view of the 1-D helical chain showing pair of right-handed helical (Ag-L_a³-)_n chains in **3a** and (c) top view of the helical chain. Symmetry codes, A: x + 1, y, z; B: x + 1/2, 3/2 - y, -z.

which the Ag¹ ion is coordinated by three S donors of three distinct L_a^3 ligands and one O atom of ClO₄⁻, showing highly distorted tetrahedral (or distorted triangle pyramid) coordination geometry. The Ag1–O3 distance of 2.53(2) Å lies in the normal Ag–O bond length range,¹⁸ and the average length of Ag–S bonds [2.538(2) Å] is also normal, but the Ag1–S1 bond distance [2.544(2) Å] is slightly longer than that of Ag1–S2A [2.504(2) Å] due to S1 adopting μ_2 -bridging coordination mode while S2 adopts a monodentate terminal coordination mode (*vide infra*). Three S–Ag–S bond angles range from 111.40(8) to 125.85(8)°, and the Ag¹ is 0.123(1) Å above the S₃ coordination plane.

Similar to those in 2a, the S donors of the ligands L_a³ also adopt μ_2 -bridging and monodentate terminal coordination modes. The whole chain can be described as two single helical chains bound together by μ_2 -S donors (Fig. 3(b), (c)). In each single chain, the ligands bridge Ag^I centers in bis-monodentate coordination mode to form right-handed single helix $(Ag-L_a^3-)_n$, which are intertwined themselves with a period of 7.506(2) Å, viz. the shortest intrachain Ag · · · Ag distance in the chain. Two such helical single chains are linked together (in couple and slippage along the chain) by μ_2 -bridging S donors of ligands to form a double chain. Interestingly, based on the μ_2 -S bridging Ag^I ions, a left-handed chiral helical chain entity $(Ag-S-)_n$ related by a 2_1 screw axis is also formed, simultaneously. In the whole helical chain, the Ag^I ions arrange in two lines and the shortest distance is 4.429(1) Å. It should also be pointed out that in the crystal structure of 3a, such helical chains arrange parallel along the crystallographic a axis, and the molecule crystallizes in chiral $P2_12_12_1$ space group. The origin of the chirality can probably be explained as that in the chain, two S atoms of each ligand all adopt S configuration when coordinated to Ag^I ions, therefore, the resultant chain, as a whole, is also chiral.

 $\{[Ag(L_a^4)_2]CIO_4\}_a$ 4a, a 2-D framework. 4a is 2-D coordination network containing cationic layers with left- and righthanded single helical chains and CIO_4^- anions. As shown in Fig. 4(a), each Ag¹ center involves in a distorted tetrahedral coordination geometry comprising four S donors from four distinct L_a^4 ligands with S-Ag-S bond angles ranging from 100.6(1) to 116.4(1)°. The average Ag-S bond length of 2.592(3) Å is slightly longer than those of the complexes 1a-3a, probably due to the differences of the coordination geometries.

At first sight, in the cationic layer, each ligand bridges two adjacent four-coordinate Ag^I centers to form 28-membered twisted rectangular macrometallacycles, $Ag_4(L_a^4)_4$, and such repeating units are extended along the a and b directions to form a 2-D network. With a delicate observation, we can find that the ligands play two roles in the 2-D network (Fig. 4(b), (c)). First, half of the ligands link Ag^I ions to form left- and right-handed helical chains running along the b direction. In each chain Ag^{I} ions are arranged in two lines and two Ag^I and two ligands finish one whorl with the screw-pitch of 9.76(1) Å. Then these left- and right-handed helical chains are further bridged alternately by the other half of the ligands to form an achiral 2-D layer, in which the shortest inter-chain (helical single chain) Ag \cdots Ag distances are 9.621(7) Å. Similarly to those in 1a, the two S atoms of one L_a^4 ligand adopt R, S (or S, R) configuration, while the four around each Ag^{I} center are the same S or R configuration. In addition, in the crystal, the 2-D layers stack face-to-face along the c axis without offsetting, however no channel is left in the stacking direction because of the existence of the ethyl groups of ligands and the included ClO₄⁻, which is different from that in other 2-D dithioether Ag^I complexes reported in this work.

Although many chiral helix complexes have been reported,¹⁹ in **3a** and **4a**, the combination of helixes to form complicated chiral or *meso* structures are rare and interesting in chiral coordination polymers.

 $[AgL_b^{-1}ClO_4]_2$ 1b, a dinuclear complex. The structure of complex 1b consists of a $(AgL_b^{-1})_2^{2+}$ cation and two ClO_4^{-} anions which weakly coordinate to the central Ag¹ ions. As shown in



(c)

Fig. 4 (a) View of the coordination environment of Ag^{1} in **4a**, (b) the 2-D network of **4a** showing the two types of ligand linkage modes and left- and right-handed helixes and (c) view of the 2-D layer along another direction (the ethyl groups were omitted for clarity in (a) and (b)). Symmetry codes, A: 2 - x, y + 1/2, 1/2 - z; B: 1 - x, 2 - y, -z.

Fig. 5(a), in the complex cation related by a crystallographic center of symmetry, each Ag¹ is two-coordinated to two S donors from two ligands in an approximate linear geometry, and two Ag¹ ions are bridged equivalently by two ligands which adopt a bis-monodentate coordination mode to form a unique box-like dimeric entity. Two Ag–S bond distances are almost equivalent and shorter than those in other three- or four-coordinate thioether Ag¹ complexes in this work (see Table 2). The S–Ag–S bond angle is 166.65(5)°, which deviates from 180° due to the weak coordination of two perchlorate O atoms to





⁽b)

Fig. 5 (a) View of the dinuclear cationic structure of **1b** and (b) 1-D chain formed by ClO_4^- linking the dinuclear cations. Symmetry codes, A: 1 - x, 1 - y, 1 - z; B: x, y - 1, z.

the central Ag¹ ion, with the Ag–O distances being 2.639(5) and 2.639(6) Å for Ag1–O1 and Ag1–O2B, respectively. It should be noted that in the dinuclear unit, the Ag···Ag distance of 3.036(1) Å lies in the range (2.86–3.22 Å) found in similar systems,²⁰ showing weak ligand-sustained Ag–Ag interaction. In addition, in the cationic dimer the coordinated S atoms show *S*,*S* configuration for one ligand and *R*,*R* for the other, and two phenyl groups reside in the same side of each S–C–S skeleton. This arrangement may help to decrease the space hindrance.

Another interesting point is the presence of weak coordination linkages between such dinuclear cations and ClO_4^- anions. As shown in Fig. 5(b), ClO_4^- anions link the dinuclear units in bidentate bridging mode (O–Cl–O) through the weak coordination of O atoms to the central Ag¹ ions, forming a 1-D chain, in which the intermolecular Ag···Ag distance is 4.047(2) Å. In addition, the intermolecular S···S, S···Cl and S···Ag weak interactions are also observed.

 $[Ag(L_b^2)_2]CIO_4$ 2b, a mononuclear complex. Complex 2b consists of discrete $[Ag(L_b^2)_2]^+$ cations (Fig. 6) and CIO_4^- anions,



Fig. 6 The cationic structure of 2b.

and the Ag^I center is coordinated by four S donors of two L_b^2 ligands. The four Ag-S bond distances can be divided into two groups: 2.604(1), 2.590(1) and 2.515(1), 2.523(1) Å, with the average value of 2.558(1) Å, being in the normal range expected for such coordination bonds.18 The coordination geometry around each Ag¹ center can be described as a distorted tetrahedron with the S-Ag-S angles ranging from 85.17(5) to $141.27(4)^{\circ}$. The angle between the two coordination planes defined by S1-Ag1-S2 and S3-Ag1-S4 is 76.45(5)°. In 2b, two ligands bond one Ag^I center in bidentate coordination mode to form two five-membered chelate rings. It is interesting that the two ligands show different configurations, cis and trans, based on the two phenyl rings of each ligand locating at the same side or the opposite side of their corresponding coordination planes (S-Ag-S). Further, the coordinated S atoms of two ligands have different configuration, R,S for one ligand (cis), and S,S for the other one (trans).



Fig. 7 (a) View of the coordination environment of Ag^{1} and the ligand linking mode, (b) 2-D (6,3) layer structure of **3b** and (c) 3-D framework showing ClO_{4}^{-} linkages (the benzyl groups were omitted in (c)). Symmetry codes: A: 2 - y, x - y + 1, z; B: y - x + 1, 2 - x, z.

 $\{[Ag(L_b^3)_{3/2}(ClO_4)_{1/2}](ClO_4)_{1/2}\}_n$ 3b, a 3-D framework. Complex 3b has a 3-D framework structure constructed by ClO₄bridging cationic 2-D (6,3) layers $[Ag(L_b^{3})_{3/2}]^{n+}$, which are similar to those in 1a. The Ag^I center, with a threefold axis passing through it, is coordinated equivalently to three S donors from three distinct L_{b}^{3} ligands in the equatorial positions and an O atom of disordered ClO_4^- ions in the axial position (Fig. 7(a)). Thus, the Ag^I ion resides in a trigonal pyramid environment with the Ag–S and Ag–O bond lengths of 2.502(1) and 2.22(1) Å, respectively, and the S-Ag-S bond angle of 119.766(5)° (near 120°). In the cationic layer of **3b** each ligand links two Ag^I centers through two S donors in bis-monodentate bridging mode to form centrosymmetric 36-membered $[Ag_6(L_b^3)_6]$ macrometallacyclic units, in which six Ag^I ions are located alternately up and down. As in 1a, the central C atom (C9) of the ligand lies on a twofold axis. In the macrometallacycle, the distance of adjacent Ag^I ions is 9.057(2) Å and the S \cdots S distance in L_b³ is 5.545(2) Å. Eventually, the macrometallacycle extends out in a and bdirections to form a 2-D (6,3) net (Fig. 7(b)) in which the benzyl groups of ligands are located alternately up and down the layer probably for reducing the steric hindrance. Three benzyl groups around one Ag^I center lie in the same side of the whole layer and the dihedral angle between them is 77.8(2)°. Each ligand shows R, S (or S, R) configuration based on its two coordination S atoms.

In **3b**, the ClO_4^- ions are highly disordered and are located in the symmetry point, with half residing in the hexagonal $[\text{Ag}_6(\text{L}_b^3)_6]$ macrometallacyclic cavities of each layer, which may act as a template, and the other half link such layers to form a 3-D framework (Fig. 7(c)). It should also be noted that in **3b**, the 2-D layers linked by ClO_4^- ions stack in an ABC sequence along the *c* axis, and the face-to-face stacking of such sheets does not produce substantial channels viewed down the stacking direction. This is different from that in **1a**. It is also interesting that when AgNO₃ reacted with L_b^3 under similar reaction conditions, the resultant complex has the same structural features as **3b**, except for different anions.¹²⁰ This result reveals that the anions do not have an obvious influence on the structures of the Ag¹ complexes with this ligand.

 $[Ag(L_b^4)_{3/2}ClO_4]_n$ 4b, a 1-D single, double-bridging chain. 4b consists of 1-D single, double-bridging chain cations and ClO_4 anions. The Ag^I ion is trigonally coordinated to three S donors from three distinct L_b^4 ligands with Ag-S bond lengths of 2.524(2) Å (Ag1-S2) and 2.512(2) Å (Ag1-S3) for the doublebridging unit and 2.509(2) Å (Ag1-S1) for the single-bridging one (Fig. 8(a)). The sum of three S-Ag-S bond angles is 357.57(6)°, slightly deviating from 360° of the trigonal plane due to one O atom of ClO₄⁻ weakly coordinating to the Ag^I ion [the Ag1–O1 distance is 2.723(6) Å]. In **4b** a pair of Ag¹ ions are linked by two bridging L_b⁴ ligands to form binuclear 14-membered macrometallacyclic units $(AgL_{b}^{4})_{2}$. Adjacent $(AgL_{b}^{4})_{2}$ units are further linked by other ligands in single-bridging fashion to result in a single, double-bridging chain (Fig. 8(b)). The $Ag \cdots Ag$ distances within the ring unit and in single bridge one are 7.294(3) and 8.626(3) Å, respectively. The two S atoms of each one ligand show S, R (or S, R) configuration for all of them. In addition, in the crystal packing, such 1-D chains are arranged paralleling to each other along the crystallographic [1/2 0 1] direction.

Discussion

The structural differences of 1a-4b in the solid state, may be attributed to the differences of the spacer length and terminal groups of such ligands. These results further confirm that the spacers and terminal groups of ligands have great influence on the structures of their Ag^I complexes.^{12h-o} Table 3 summarizes



(a)



(b)

Fig. 8 (a) View of the coordination environment of Ag¹ and (b) 1-D single, double-bridging chain structure of **4b**. Symmetry codes: A: -x, -y, -z; B: 1 - x, -y, 1 - z.

 Table 3
 Structural comparisons of Ag¹ complexes with structurally related flexible dithioether ligands

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Compound	Formula	Ag ¹ Geometry (No.)	Ligand coord. modes	Ag–S length (av.)/Å	Ag–O length/Å	Structural features	Ref.
1 a	$[\mathrm{Ag}(\mathbf{L_a}^1)_{3/2}\mathrm{ClO_4}]_n$	Trigonal pyramidal (4)	Bis-monodentate bridging	2.509(1)	2.589(7)	2-D (6,3) layer containing [24]-rings, stacking in ABAB mode to form quasi 3-D framework showing small channels	This work
2a	$[Ag_2(L_a^2)_2(CIO_4)_2]_2$	Linear (2), tetrahedral (4)	Chelating combining μ2-bridging	2.456(2), 2.587(2)	2.648(5), 2.67(2), 2.68(1)	Tetranuclear (Ag–S–) $_4$ rings, being further linked to form 2-D (4,4) net through CIO ₄ ⁻ weak coordination	This work
3a	$[\mathrm{AgL}_{\mathrm{a}}{}^{3}\mathrm{ClO}_{4}]_{n}$	Tetrahedral (4)	Monodentate combining ۱۱۰hridoino	2.538(2)	2.53(2)	1-D chiral helical chain containing two right-handed (Ao-I-) and one left-handed (Ao-S-) chains	This work
4a	$\{[\operatorname{Ag}(\mathbf{L_{a}}^{4})_{2}]\operatorname{ClO}_{4}\}_{n}$	Tetrahedral (4)	Bis-monodentate bridging	2.592(3)		2-D sheet containing [28]-rings, formed by L linking left- and right-handed (Ag-L-), helical chains, alternately	This work
1b	$[AgL_{h}^{1}CIO_{4}]_{2}$	Trigonal planar (3)	Bis-monodentate bridging	2.444(2)	2.639(5)	Dinuces [8]-rings showing ligand-sustained Ag-Ag interaction, being further linked to form 1-D chain through	This work
2b 3b	$[Ag(L_b^2)_2]CIO_4 \\ [Ag(L_b^3)_{3/2}(CIO_4)_{1/2}]^{-1}$	Tetrahedral (4) Trigonal pyramidal (4)	Bis-monodentate chelating Bis-monodentate bridging	2.558(1) 2.502(1)	2.22(1)	 CIO4 weak concutation Mononuclear containing chelating [5]-rings 3-D framework formed by CIO4⁻ bridging 2-D (6,3) layer containing [36]-rinos 	This work This work
4b 1c 2c	$[\operatorname{Ag}(\mathbf{L}_{0}^{4})_{3/2}]^{n}$ $[\operatorname{Ag}(\mathbf{L}_{0}^{4})_{3/2}]C[0_{4}]_{n}$ $[\operatorname{Ag}(\mathbf{L}_{c}^{2})_{3/2}C[0_{4}]_{n}$	Trigonal pyramidal (4) Trigonal planar (3) Trigonal pyramidal (4)	Bis-monodentate bridging Bis-monodentate bridging Bis-monodentate bridging	2.515(2) 2.549(2) 2.532(1)	2.723(6) 3.012(2) 2.782(1),	1-D single, double-bridging chain containing [14]-rings 3-D chiral non-interpenetrated (10,3)-a net 2-D (6,3) layer	This work 12k 12n
3c"	$\{[\operatorname{Ag}(\mathbf{Lc}^3)_2]\operatorname{BF}_4\}_n$	Tetrahedral (4)	Bis-monodentate bridging	2.589(3)	(1)c±c	3-D non-interpenetrated framework containing [24]-rings	12 <i>h</i>
5 5 2	$\{ [Ag(Lc^{2})_{3/2}]CIO_{4} \}_{n} $ $\{ [Ag(Lc^{5})_{2}]CIO_{4} \}_{n} $	1 rigonal planar (3) Tetrahedral (4)	Bis-monodentate bridging Bis-monodentate bridging	2.519(6) 2.619(5)	2.932(6) —	2-D honeycomb-like (6,3) layer containing [42]-rings 2-D (4,4) lattice containing [32]-macrocycles	121 12m
66	$[AgL, CO_4]_2$	Tetrahedral (4)	Bis-monodentate bridging	2.520(2)	2.48(1), 2.52(1)	Centrosymmetric dinuclear cage made up of [18]-(Ag-L-), macrocycle and [8]-(Ag-C1O,-), ring	12 <i>i</i>
1d	$[AgL_{d}^{1}ClO_{4}]_{n}$	Trigonal planar (3)	Bis-monodentate bridging	2.415(2)	2.662(2), 2.760(2)	1-D single-bridging zigzag (Ag-L-), chain, combining (Ag-C10,-), chain to form double-bridging chain	12j
2d 3d	[Ag(L _a ²) _{3/2} ClO ₄] _n {[AgL ₃ ³]ClO ₄ },	Trigonal pyramidal (4) Ouasi-linear (2)	Bis-monodentate bridging Bis-monodentate bridging	2.527(5) 2.412(2)	2.797(4) 2.941(2)	2-D (6.3) L mark containing [30]-rings Centrosymmetric dinnelear [12]-macrometa llacocle	12 <i>j</i> 12 <i>j</i>
5d 4d	$[AgL_{4}^{5}CIO_{4}]_{3/2}$	Trigonal pyramidal (4) Tetrahedral (4)	Bis-monodentate bridging Bis-monodentate bridging	2.569(2) 2.467(1)	2.711(2)	Single, double-bridging chain containing [16]-rings Centrosymmetric dinuclear [16]-macrometallacycle,	12 <i>j</i> 12 <i>j</i>
6d	$[Ag(L_{\mathfrak{a}}^{\mathfrak{6}})_{3/2}ClO_4]_{n}$	Tetrahedral (4)	Bis-monodentate bridging	2.531(3)	2.783(1) 2.470(9)	combining [8]-(Ag-CIO ₂ -), ring to torm cage 1-D single, double-bridging chain containing [18]-rings	12 <i>j</i>

"Here, we speculate on { $[Ag(L^{9})_{1}]BF_{4}$, and { $[Ag(L^{9})_{1}]CIO_{4}$, having similar structures, for the comparison. $L_{a}^{1} = bis(ethylthio)methane, <math>L_{a}^{2} = 1,2$ -bis(ethylthio)propane, $L_{a}^{3} = 1,3$ -bis(phenylthio)propane, $L_{a}^{4} = 1,4$ -bis(phenylthio)putane, $L_{a}^{2} = 1,2$ -bis(benzylthio)putane, $L_{a}^{2} = 1,2$ -bis(phenylthio)putane, $L_{a}^{2} = 1,5$ -bis(phenylthio)pentane, $L_{a}^{4} = 1,4$ -bis(phenylthio)putane, $L_{a}^{2} = 1,5$ -bis(phenylthio)pentane, $L_{a}^{4} = 1,4$ -bis(phenylthio)putane, $L_{a}^{2} = 1,5$ -bis(phenylthio)pentane, $L_{a}^{4} = 1,6$ -bis(phenylthio)hexane, $L_{a}^{1} = bis(terr-butylthio)methane, <math>L_{a}^{2} = 1,5$ -bis(phenylthio)pentane, $L_{a}^{4} = 1,4$ -bis(terr-butylthio)putane, $L_{a}^{4} = 1,5$ -bis(terr-butylthio)pentane, $L_{a}^{4} = 1,6$ -bis(terr-butylthio)hexane, $L_{a}^{1} = 1,2$ -bis(terr-butylthio)butane, $L_{a}^{2} = 1,5$ -bis(terr-butylthio)pentane, $L_{a}^{4} = 1,6$ -bis(terr-butylthio)hexane.

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the basic structural parameters and features for four series of the complexes with structurally related dithioether ligands (Chart 1), which helps to examine the effects of some alterable factors on the structures of such complexes. The structural differences of such complexes imply that the flexible –(CH₂)_n– backbone can allow the ligands to rearrange so as to minimize the steric hindrance when coordinated to metal ions, leading to the conformational variation of such ligands to result in the structural diversities of their complexes. It should also be noted that the coordination behavior of the ligands with \mbox{AgClO}_4 is flexible and diverse. The S atom in thioether ligands has two lone electron pairs, which can take part in coordination to metal ions. In these complexes the S donors adopt monodentate and μ_2 -S bridging modes, and the former is prior to the latter, probably for reducing the steric hindrance. In addition, the Ag-S bond distance increases with the increasing of the number of the coordinated S atom around Ag^I (Fig. 9).



Fig. 9 Graphic presentation of the relationship between Ag^{I} coordination number with S and Ag–S bond length in the twenty complexes.

In conclusion, eight dithioether– Ag^{I} metal–organic architectures with different structures have been constructed by selfassembly of AgClO₄ with two series of dithioether ligands that are related in structure, and a variety of coordination modes of Ag^I and the ligands were observed. Comparison with the structures of other AgClO₄ complexes of closely related ligands further indicates that the structures of such complexes could be adjusted by the ligand spacers and terminal groups. Such results present a feasible way for varying the structures of complexes by modifying the ligand spacers and terminal groups. In addition, other factors such as the diversity of the Ag^I coordination, the flexibility of the ligands, and the variable coordination modes of S donors also play important roles in affecting the framework formations of such complexes.

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