NJC

Accepted Manuscript

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Supramolecular silver(I) coordination isomers of different dimensionalities assembled by a conformationally flexible multidentate oligo-α-sulfanylpyrazinyl ligand

Comment [TCWMak1]: Textual changes are highlighted in yellow.

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Abstract

Three genuine supramolecular isomers and one homologous complex based on a conformationally flexible multidentate 2,6-bis(pyrazin-2-ylthio)pyrazine (**L**) ligand, namely α-[Ag(**L**)ClO$_4$]$_n$ (**1a**), β-[Ag(**L**)ClO$_4$]$_n$ (**1b**), γ-[Ag(**L**)ClO$_4$]$_n$ (**1c**) and [Ag$_2$(**L**)$_3$(ClO$_4$)$_2$·2H$_2$O]$_n$ (**2**), have been synthesized and structurally characterized by single-crystal X-ray diffraction analyses. Isomers **1a**-**1c** feature a chain, sheet and three-dimensional framework, respectively. Compound **2** shows a ladder-like structure with an unusual zigzag water chain. In these complexes, ligand **L** exhibits four distinct coordination modes and stereochemical conformations, and their effects on the formation of supramolecular isomers are discussed in detail.

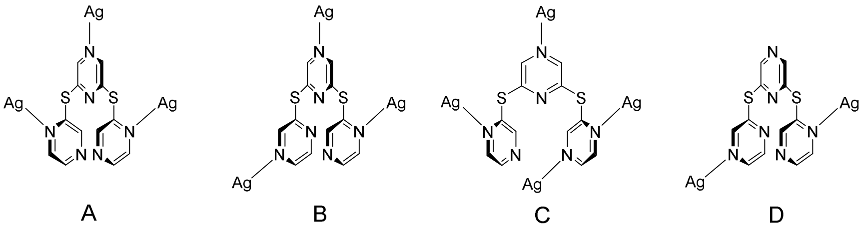
Keywords: 2,6-Bis(pyrazin-2-ylthio)pyrazine / Conformation / Coordination modes / Crystal structure / Supramolecular isomers

Introduction

Supramolecular isomerism, which refers to the existence of more than one type of network superstructures for the same chemical composition, has attracted considerable interest of chemists in fields of crystal engineering, solid-state chemistry and materials science.[1] This phenomenon affords a good opportunity for developing novel materials as well as a fundamental understanding of self-assembly and crystal growth.[2] To date, although supramolecular isomers have been extensively reported in the literature, a substantial number of them are pseudo-isomers because of the co-existence of guest components.[1a, 3] Examples of genuine isomers which exactly share the same chemical formula are rather limited.[4] A survey of the literature also reveals that coordination compounds rarely crystallize in isomeric forms, and the highest number of genuine isomers is 4 in one instance[4c] and 3 in a few cases. In particular, genuine coordination isomers in each authenticated case that exhibit more than two different dimensionalities are exceedingly rare.

Hitherto supramolecular coordination isomers have been successfully constructed utilizing flexible nitrogen-donor ligands coordinated to metal centers.[3h, 4a, 4e] The known examples indicate that the variable stereochemical conformations and coordination modes of such ligands play important roles in generating supramolecular isomers to a large extent.[4] For example, the flexible ligand 1,4-bis(2-pyridylmethyleneaminomethyl)benzene reacts with $AgClO_4$ to furnish two genuine supramolecular isomers by adopting different conformations.[3h] However, to our knowledge, the coordination modes of a conformationally flexible multidentate nitrogen-donor ligand that dominates the formation of supramolecular isomers are rarely observed.[4c] In recent years, the ligand behavior of oligo-α-sulfanylheteroaromatic compounds has attracted increasing attention in coordination chemistry.[5] In our previous work, we designed and synthesized a new ligand of this type, namely 2,6-bis(pyrazin-2-ylthio)pyrazine (abbreviated as **L)** (Scheme 1), which was found to display diverse coordination modes and flexible configurations in its silver(I) complexes.[6]

Prompted by the premise that supramolecular coordination isomers could be generated from **L**, we have carried out a one-pot synthesis and structural characterization of four related supramolecular complexes, namely α-[Ag(**L**)ClO_4]$_n$ (**1a**), β-[Ag(**L**)ClO_4]$_n$ (**1b**), γ-[Ag(**L**)ClO_4]$_n$ (**1c**) and [Ag_2(**L**)$_3$(ClO_4)$_2\cdot 2H_2O$]$_n$ (**2**). Compounds **1a**-**1c** are supramolecular coordination isomers that display distinct one-, two- and three-dimensional structures. The hydrated homologue **2** features a ladder-like crystal structure incorporating an unusual zigzag water chain. The roles played by the coordination modes and conformations of ligand **L** in the construction of supramolecular isomers **1a**-**1c** are also discussed in detail.



Scheme 1 Observed coordination modes of ligand **L** in **1a**-**1c** and **2**.

Experimental section

Materials and physical measurements

All chemical reagents were obtained from commercial resources and used without further purification. 2,6-Bis(pyrazin-2-ylthio)pyrazine (**L**) was synthesized following the procedure reported by us recently.[6a] IR spectra were recorded on a Perkin-Elmer Spectrum RX I FTIR spectrometer as KBr pellets in the range of 4000-400 cm^{-1} with a resolution of 2 cm^{-1} at room temperature. Elemental analysis (C, H, N) was performed by the Analysis and Testing Center of Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

Syntheses of complexes

A mixture of 2,6-bis(pyrazin-2-ylthio)pyrazine (**L**) (30 mg, 0.1 mmol) and $AgClO_4$ (42 mg, 0.2 mmol) was dissolved in a mixed solvent of 3 mL acetonitrile and 3 mL deionized water at room temperature. After stirring for about 3 hours, the pale-yellow solution was filtrated and allowed to stand in the dark for slow evaporation. After about one week, yellow crystalline blocks of **1a**, needles of **1b**, prisms of **1c**, and plates of **2** deposited together from the mother liquor. Complexes **1a**-**1c** and **2** were obtained in *ca.* 5%, 32%, 6% and 5% yield, respectively, based on ligand **L**. The major product was **1b**, while co-crystallized **1a**, **1c** and **2** of distinguishable morphology were handpicked for single-crystal X-ray analysis. Elem. Anal. Calcd (Found) for **1a:** $C_{12}H_8AgClN_6O_4S_2$: C, 28.39 (27.57); H, 1.59 (1.66); N, 16.55 (16.10) %; IR (KBr) ν/cm^{-1} for **1a**: 3457(vs), 1631(s), 1498(s), 1457(m), 1391(s), 1289(w), 1186(m), 1137(vs), 1121(vs), 1081(s), 1047(m), 1012(s), 998(w), 842(w), 797(w), 636(s), 625(s); Elem. Anal. Calcd (Found) for **1b**: $C_{12}H_8AgClN_6O_4S_2$: C, 28.39 (27.68); H, 1.59 (1.61); N, 16.55 (16.13) %; IR (KBr) ν/cm^{-1} for **1b**: 3454(s), 1628(m), 1497(vs), 1457(s), 1385(vs), 1289(m), 1185(s), 1135(vs), 1122(vs), 1109(vs), 1079(vs), 1047(m), 1011(s), 998(w), 842(m), 827(m), 636(m), 625(m); Elem. Anal. Calcd (Found) for **1c**: $C_{12}H_8AgClN_6O_4S_2$: C, 28.39 (27.94); H, 1.59 (1.47); N, 16.55 (16.20) %; IR (KBr) ν/cm^{-1} for **1c**: 3447(s), 1636(w), 1497(s), 1457(s), 1392(s), 1290(w), 1183(m), 1136(vs), 1087(vs), 1046(m), 1012(s), 842(m), 827(m), 758(w), 636(m), 625(s); Elem. Anal. Calcd (Found) for **2**: C, 31.99 (31.27); H, 2.09 (2.21); N, 18.65 (17.13) %; IR (KBr) ν/cm^{-1} for **2**: 3447(s), 1636(w), 1497(s), 1457(s), 1392(s), 1290(w), 1184(m), 1136(vs), 1121(vs), 1086(vs), 1048(s), 1012(s), 999(m), 844(m), 826(m), 758(w), 636(m), 625(s).

X-ray crystallographic studies

Single-crystal X-ray diffraction data of all four compounds were collected on a Bruker Kappa APEX II CCD diffractometer operating at 50 kV and 30 mA using Mo-*Kα* radiation (λ = 0.71073 Å) at 293 K (Table 1). The structures were solved by direct methods with SHELX-97[7] and refined by full-matrix least-squares techniques using the SHELXL-97[8] program within WINGX.[9] The ordered atoms in each structure were refined with anisotropic displacement parameters, while the hydrogen atoms were placed in idealized positions and allowed to ride on their parent carbon atoms. The H atoms of water molecules of **2** were located from Fourier maps. Selected bond lengths are listed in Table 2.

Results and discussion

Role of solvent in synthesis

Complexes **1a**-**1c** and **2** were synthesized from a one-pot reaction of ligand **L** and $AgClO_4$ in a mixed solution of water and acetonitrile. Although **1b** was found to be the main product, **1a**, **1c** and **2** also appeared as byproducts in low yields. However, if the reaction was carried out in acetonitrile, solvent evaporation or diffusion of diethyl ether into the reaction system gave **1b** as the only product.

Structural descriptions of 1a-1c and 2

Crystal structure of α-$[Ag(L)ClO_4]_n$ (1a). Complex **1a** crystallizes in monoclinic space group $P2_1/c$, and the asymmetric unit corresponds to its stiochiometric formula. Each Ag(I) atom is located in a trigonal coordination environment composed of three N atoms from independent **L** ligands (Ag1−N1 = 2.367(4), Ag1−N4A = 2.268(3) and Ag1−N5B = 2.306(3) Å). As shown in Fig. 1a, ligand **L** adopts μ_3-*N*,*N′*,*N″* coordination mode A (Scheme 1) with the two 2-positional N atoms (N1 and N5) on the pendant pyrazinyl groups in an *exo* relationship with respect to the central ring. Adjacent Ag(I) atoms are linked by **L** to yield a coordination ribbon extending along the *a* axis (Fig. 1b). In addition, weak interactions between perchlorate O atoms and Ag(I) atoms[10] occur with Ag1···O1 = 2.885(5) and Ag1···O2 = 2.921(4) Å, linking the coordination ribbons to give a 3D supramolecular architecture (Fig. 1c).

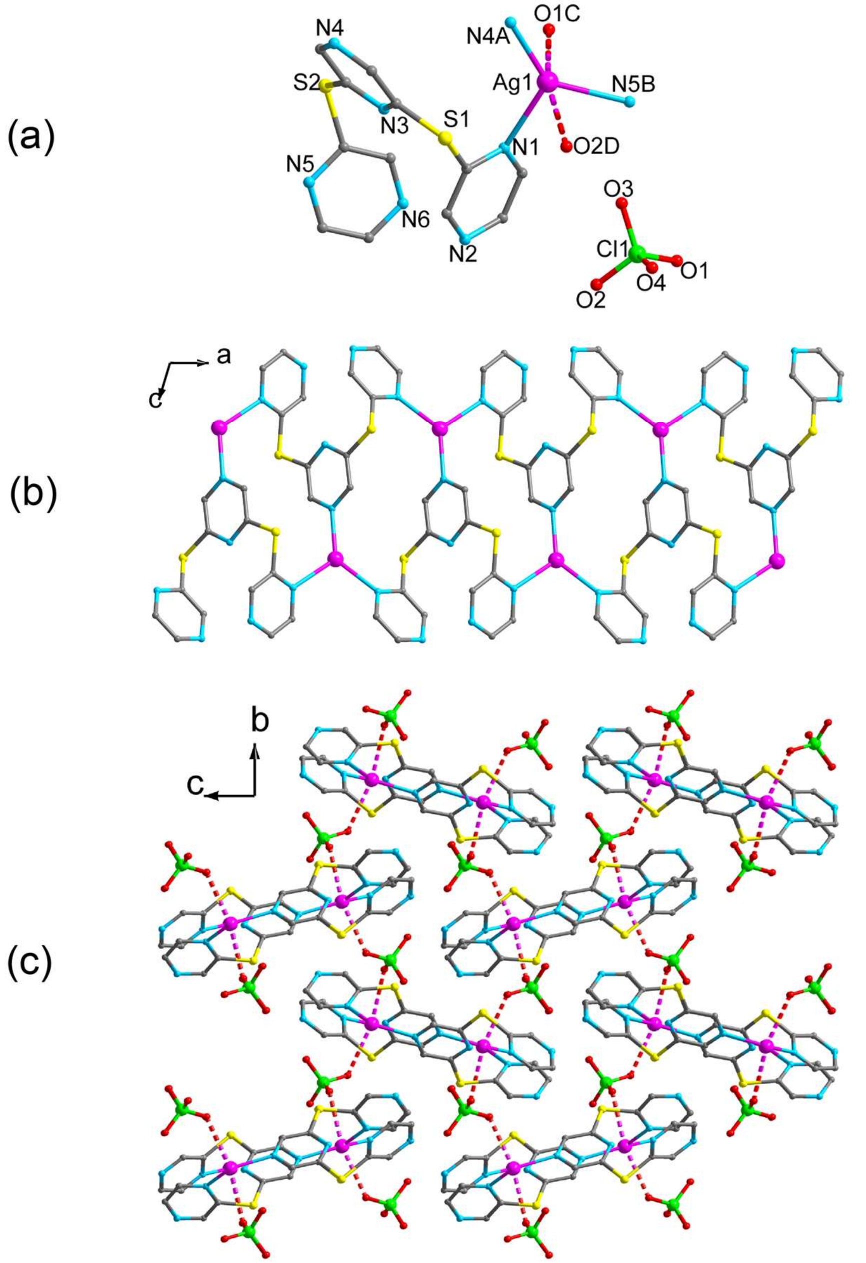


Fig. 1 (a) The asymmetric unit of **1a**. Symmetry codes: A –*x*, –*y*, –*z*; B *x* + 1, *y*, *z*. C –*x* +1, –*y*, –*z* + 1; D *x*, –*y* + 0.5, *z* – 0.5. (b) Coordination ribbon in the crystal structure of **1a**.

(c) 3D Supramolecular architecture of **1a** viewing along the *a* axis. Weak Ag···O interactions are shown by dashed lines. Hydrogen atoms are omitted for clarity. Color codes: C, gray; O, red; N, sky blue; S, yellow; Ag, violet.

Crystal structure of *β*-[Ag(L)ClO$_4$]$_n$ (1b). Isomer **1b** crystallizes in orthorhombic space group $P2_12_12_1$. Each Ag(I) atom is in a distorted tetrahedral N$_3$O environment involving different kinds of N atoms of **L** and a perchlorate O atom (Ag1−N1 = 2.313(3), Ag1−N4A = 2.377(2), Ag1−N5B = 2.235(2) and Ag1−O1 = 2.671(4) Å) (Fig. 2a). Ligand **L** takes μ_3-*N*,*N*′,*N*″ bridging mode B (Scheme 1), bridging neighboring Ag(I) atoms to afford a wavy sheet, with perchlorate anions attached to it on both sides (Fig. 2b). Topologically, this sheet can be considered as a 2D (6,3) net by treating both the Ag(I) atom and ligand **L** as 3-connected nodes (Fig. 2c). Moreover, *π*-*π* interactions exist between the N4-containing pyrazinyl ring and the N6-containing pyrazinyl ring on adjacent sheets (centroid–centroid distance = 3.474(2) Å and dihedral angle = 1.2(1) °), resulting in a 3D supromolecular architechture (Fig. 2d).

It should be pointed out that ligands **L** in **1a** and **1b** show different coordination modes and conformations. In **1a**, **L** adopts coordination mode A involving both 2-positional N atoms on the pendant pyrazinyl rings. Nevertheless, in **1b**, one 2-positional and one 5-positional N atoms on the pendant rings act as coordination sites. In addition, ligand **L** exhibits different conformations: the two 2-positional N atoms are in an *exo* relationship with respect to the central ring in **1a**, while the two 2-positional N sites on the corresponding pyrazinyl rings of **L** in **1b** are in an *endo* relationship (Scheme 1). It is clear that the coordination modes and conformations of ligands **L** are the dominant factors for formation of the two supramolecular isomers with different dimensionalities.

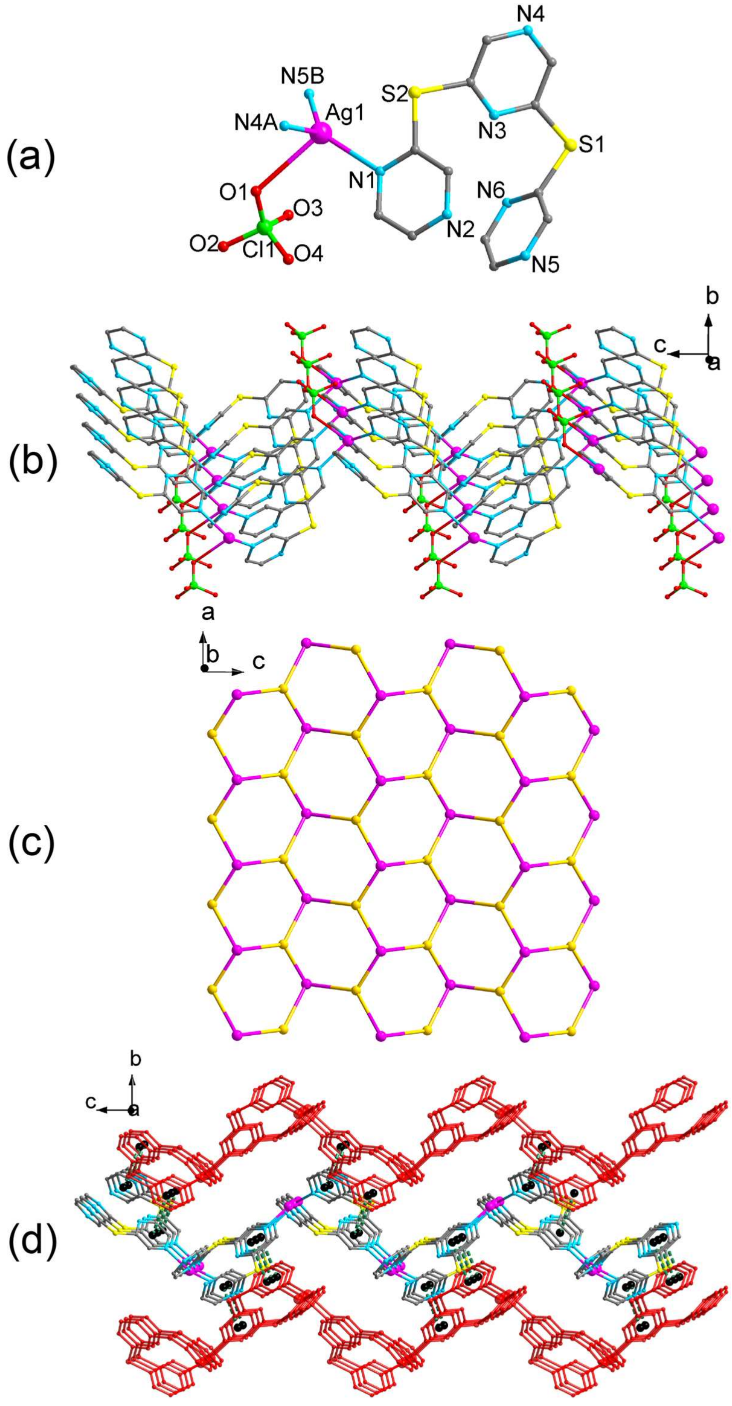

(a)
N4
N5B
S2
Ag1
N4A
N3
S1
O1
N1
N6
O3
O2
Cl1
O4
N2
N5
(b)
b
c
a
a
b
c
(c)
b
c
a
(d)

Fig. 2 (a) The asymmetric unit of **1b**. Symmetry codes: A *–x* – 0.5, *–y*, *z* + 0.5; B *x* – 1, *y*, *z*. (b) Wavy sheet in the crystal structure of **1b**. (c) Idealized 2D (6,3) net. (d) Packing of coordination sheets with π-π interactions illustrated as green broken lines. Hydrogen atoms are omitted for clarity. Color codes: C, gray; O, red; N, sky blue; S, yellow; Ag, violet.

Crystal structure of γ-[Ag(L)ClO$_4$]$_n$ (1c). Isomer **1c** crystallizes in orthorhombic space group $P2_12_12_1$, and its asymmetric unit also matches its stoichiometric formula (Fig. 3a). Each Ag(I) atom is coordinated by four N atoms from individual **L** ligands (Ag1−N4 = 2.489(5), Ag1−N1A = 2.344(5), Ag1−N2B = 2.342(4) and Ag1−N5C = 2.654(4) Å). Ligand **L** taking μ_4-*N*,*N'*,*N''*,*N'''* coordination mode C (Scheme 1) links four Ag(I) atoms to yield a 3D coordination framework (Fig. 3b). From the topological point of view,[11] if ligand **L** and Ag(I) atom are defined as individual 4-connected nodes, the 3D topological framework of **1c** can be regarded as a 4-connected, uni-nodal **sra** net with the short 4^26^38 Schläfli symbol (Fig. 3c). The perchlorate anions are trapped in the channels of the 3D framework with a weak Ag···O interaction between Ag1 and O2 (Ag1···O2 = 2.771(4) Å).

Notably, ligand **L** adopts μ_4 mode C by employing an additional N atom on the pendant pyrazinyl ring as a coordination site, rather than the μ_3 modes A and B. As a result, a 3D coordination framework is formed in **1c**, which differs entirely from the chain in **1a** and the sheet in **1b**. Clearly the coordination modes of ligands **L** dictate the formation of isomeric complexes as well as their coordination dimensionality.

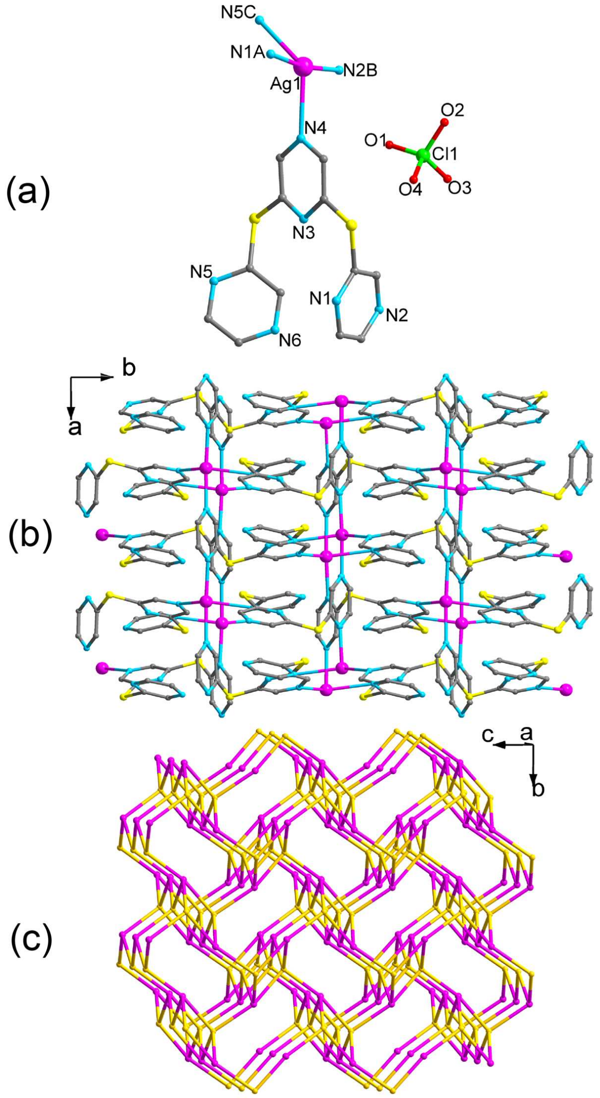


Fig. 3 (a) The asymmetric unit of **1c**. Hydrogen atoms are omitted for clarity. Symmetry codes: A –*x* + 1, *y* – 0.5, –*z* + 0.5; B –*x* + 2, *y* – 0.5, –*z* + 0.5; C –*x* + 1.5, –*y*, *z* – 0.5. (b) 3D framework constructed by Ag(I) centers and ligands **L**. Hydrogen atoms and uncoordinated perchlorate anions are omitted for clarity. Color codes: C, gray; O, red; N, sky blue; S, yellow; Ag, violet. (c) The 3D **sra** topological framework of **1c**.

Crystal structure of [$Ag_2(L)_3(ClO_4)_2 \cdot 2H_2O]_n$ (2). Complex **2**, obtained together with isomeric **1a-1c** from a one-pot reaction, crystallizes in monoclinic space group $P2_1$ with its asymmetric unit corresponding to its stoichiometric formula. Each independent Ag(I) atom is coordinated by three N atoms from adjacent ligands **L** in trigonal planar geometry (Ag1−N1 = 2.217(7), Ag1−N7 = 2.351(6), Ag1−N5A = 2.340(8), Ag2−N12 = 2.458(7), Ag2−N13 = 2.251(8) and Ag2−N18A = 2.210(6) Å) (Fig. 4a). Each ligand **L** adopts μ_2-*N*,*N′* coordination mode D (Scheme 1). In this way, adjacent Ag(I) atoms are linked by **L** to form a ladder extending along the *b* axis (Fig. 4b). Each rung of the ladder is composed of one N9-containing **L**, and each section of the sides consists of one N3- and N15-containing **L** ligand. Adjacent coordination ladders interact through π-π interaction between the N1- and N3-containing pyrazinyl rings (centroid–centroid distance = 3.449(5) Å and dihedral angle = 7.4(4) °), as well as between the N15- and N17-containing rings (centroid–centroid distance = 3.628(5) Å and dihedral angle = 9.5(4) °), to afford a supramolecular layer in the (−102) plane (Fig. 4c). Lattice water molecules and perchlorate anions are intercalated into adjacent supramolecular layers. As shown in Fig. 4d, water molecules O1W and O2W are connected alternately by hydrogen bonds to furnish zigzag water chains extending along the *b* axis. The $O_{water} \cdots O_{water}$ distances found in these water chains are 2.78(1) and 2.80(1) Å, which are close to the O···O distances in ice I_c (2.75 Å) and I_h (2.759 Å) determined at –130 and –90 °C, respectively.[12] Each water chain is further stabilized by Cl2-containing perchlorate anions *via* hydrogen bonding interactions with $O_{water} \cdots O$ distances of 2.97(1) and 2.99(2) Å. Interestingly, weak contacts occur between Ag1 atoms and O8 atoms of the Cl2-containing perchlorate anions with Ag···O distance of 2.81(1) Å. Finally, the supramolecular layers are extended by these weak supramolecular interactions (O_{water}···$O_{perchlorate}$, O_{water}···O_{water} and Ag···$O_{perchlorate}$) to yield a 3D supramolecular architecture (Fig. 4e).

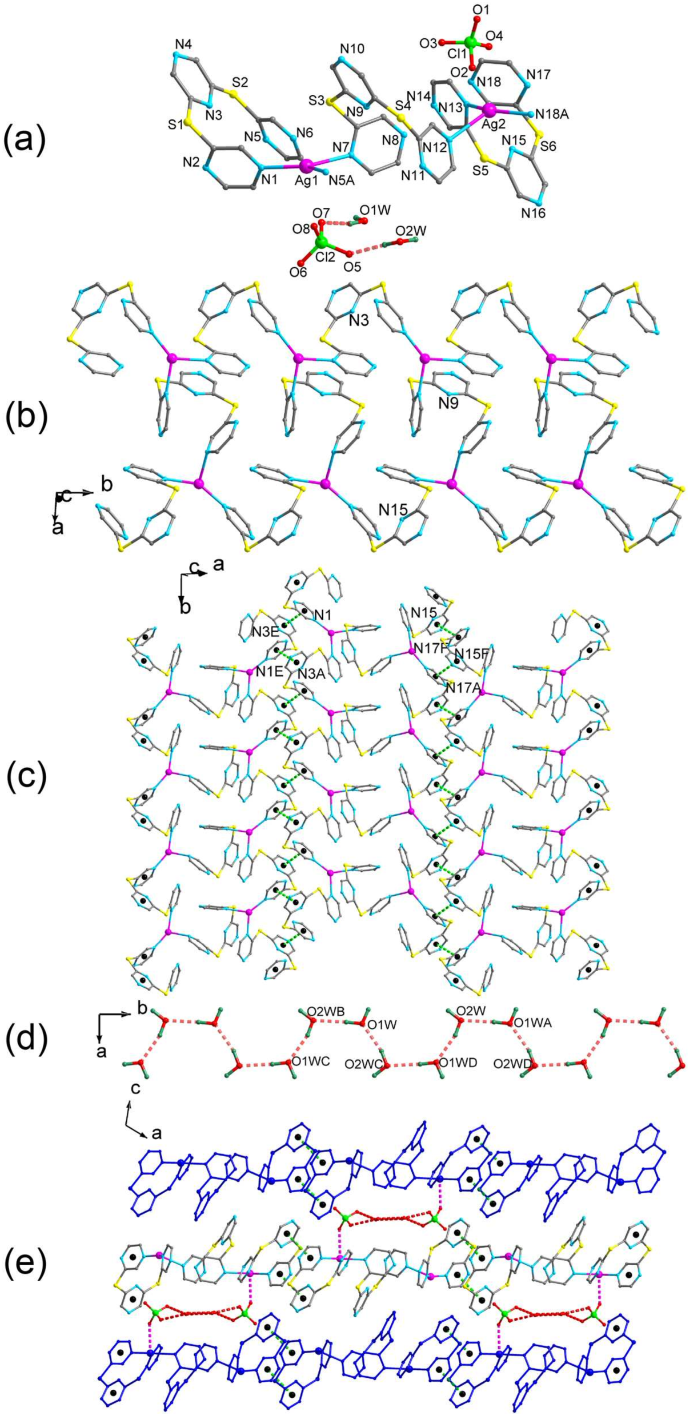

(a)
N4
S2
N3
S1
N5
N6
N2
N1
Ag1
N5A
N7
N10
S3
N9
S4
N8
N14
N13
N12
N11
O1
O3
O4
Cl1
O2
N18
N17
Ag2
N18A
N15
S6
S5
N16
O7
O1W
O8
O2W
Cl2
O5
O6
(b)
N3
N9
N15
c
b
a
(c)
c
a
b
N1
N3E
N1E
N3A
N15
N17F
N15F
N17A
(d)
b
a
O2WB
O1W
O2W
O1WA
O1WC
O2WC
O1WD
O2WD
c
a
(e)

Fig. 4 (a) The asymmetric unit of complex **2**. (b) The coordination ladder formed in **2**. (c) Supramolecular layer composed of the coordination ladders in **2** with π-π interactions shown as green dashed lines. (d) The zigzag water chain formed by O1W and O2W. (e) The 3D supramolecular architecture formed by weak Ag···O contact and hydrogen bonding interaction illustrated by violet and red dashed lines, respectively. Hydrogen atoms are omitted for clarity. Symmetry codes: A x, $y + 1$, z; B x, $y - 1$, z; C $-x + 2$, $y - 0.5$, $-z + 2$; D $-x + 2$, $y + 0.5$, $-z + 2$. Color codes: Color codes: H, green; C, gray; O, red; N, sky blue; S, yellow; Ag, violet.

Effects of coordination modes and conformations of ligands L on the formation of supramolecular isomers

Supramolecular isomers **1a**-**1c** vary in dimensionalities from 1D to 3D. Ligands **L** in **1a**-**1c** adopt three coordination modes (modes A-C in Scheme 1), where the two pendant pyrazinyl rings of **L** in each mode take an *anti* relationship. Isomer **1a** displays a coordination chain, wherein two 2-positional N atoms on the pendant pyrazinyl rings and one 5-positional N atom on the central ring of **L** are utilized as coordination sites (mode A in Scheme 1). Isomer **1b** exhibits a coordination sheet with ligand **L** adopting coordination mode B, in which the 5-positional N atom on one pendant ring of **L** is involved in coordination to silver(I) instead of the 2-positional N on the same ring. Isomer **1c** reveals a 3D coordination framework, which is distinct from the chain of **1a** and the sheet of **1b**. In contrast to μ_3-bridging mode B, ligand **L** in **1c** adopts coordination mode C by using one additional 2-positional N site on the pendant pyrazinyl ring. It is also notable that **L** shows two stereochemical conformations in the three isomeric complexes. In **1a**, the two 2-positional N atoms on the pendant pyrazinyl rings of **L** are in an *exo* relationship with respect to the central ring, while in **1b** and **1c** the two corresponding N sites of **L** bear an *endo* relationship. It is clear that the conformation of the **L** is an important factor that leads to structural diversity of the generated isomers. Additionally, homologous complex **2** shows a ladder-like structure in which **L** adopts μ_2-bridging mode D, where the two 2-positional N atoms on the pendant pyrazinyl rings take an *endo* relationship similar to that in **1b** and **1c**. In contrast to mode B of **L** in **1b**, the 5-positional N site on the central ring of **L** in **2** (mode D) does not participate in coordination to silver(I) (Scheme 1). It is noted that complex **1a** crystallizes in the achiral space group $P2_1/c$, where the two 5-positional N sites on the two pendant pyrazinyl rings of **L** are symmetrically used as coordination sites. In contrast, **1b**, **1c** and **2** all crystallize in the same chiral space group $P2_12_12_1$, and the N sites on the pendant pyrazinyl rings of **L** are unsymmetrically employed as coordination sites.[13] These results indicate that the coordination modes and conformations of ligands **L** together play a crucial role in affecting the assembly and chirality of supramolecular isomers as well as the related homologous complex.

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Conclusions

Three silver(I) coordination isomers exhibiting 1D, 2D and 3D supramolecular frameworks, as well as one homologous complex, have been synthesized from the reaction of $AgClO_4$ with 2,6-bis(pyrazin-2-ylthio)pyrazine ligand **L** *via* a one-pot reaction in acetonitrile and de-ionized water at room temperature. The results indicate that highly flexible multidentate nitrogen-donor ligands, *via* their diverse coordination modes and variable conformations, are potentially useful for the generation of isomeric complexes exhibiting rich structural and dimensional diversity.

Electronic supplementary information

Electronic Supplementary Information (ESI) available: X-ray crystallographic files in CIF format for **1a**–**1b** and **2**. CCDC 1004133-1004136. See DOI: 10.1039/b000000x/

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Acknowledgements

We gratefully acknowledge financial support by the Hong Kong Research Grants Council (GRF CUHK 402710) and the Wei Lun Foundation, as well as The Chinese University of Hong Kong for the award of a Postgraduate Studentship to H. W. and a Research Fellowship to J. Y.

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Table 1 Crystallography Data for **1a-1c** and **2**

Complex	**1a**	**1b**	**1c**	**2**
Chemical formula	$C_{12}H_8AgClN_6O_4S_2$	$C_{12}H_8AgClN_6O_4S_2$	$C_{12}H_8AgClN_6O_4S_2$	$C_{36}H_{28}Ag_2Cl_2N_{18}O_{10}S_6$
Formula Mass	507.68	507.68	507.68	1351.76
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
a/Å	9.443(5)	8.6058(17)	7.4609(5)	17.3212(8)
b/Å	12.262(7)	13.283(3)	13.3836(10)	8.3276(4)
c/Å	14.799(8)	14.427(3)	16.1104(12)	17.9892(9)
α/°	90.00	90.00	90.00	90.00
β/°	106.506(14)	90.00	90.00	111.9220(10)
γ/°	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	1643.0(15)	1649.2(6)	1608.7(2)	2407.2(2)
Space group	$P2_1/c$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
R_{int}	0.1051	0.0468	0.0901	0.1220
R_1 ($I > 2\sigma(I)$)	0.0504	0.0226	0.0461	0.0652
$wR(F^2)$ ($I > 2\sigma(I)$)	0.1150	0.0631	0.1104	0.1515
R_1 (all data)	0.0743	0.0241	0.0548	0.0906
$wR(F^2)$ (all data)	0.1270	0.0653	0.1163	0.1753
Goodness of fit on F^2	1.050	1.010	0.991	1.046
Flack parameter		-0.01(2)	0.11(4)	0.12(3)

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bwR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

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Table 2 Selected bond lengths and interatomic contacts (Å) in **1a**-**1c** and **2**

Contact	distance	contact	distance
Complex **1a**			
Ag1−N1	2.367(4)	Ag1···O1C	2.885(5)
Ag1−N4A	2.268(3)	Ag1···O2D	2.921(4)
Ag1−N5B	2.306(3)		
Complex **1b**			
Ag1−N1	2.313(3)	Ag1−N5B	2.235(2)
Ag1−N4A	2.377(2)	Ag1−O1	2.671(4)
Complex **1c**			
Ag1−N4	2.489(5)	Ag1−N2B	2.342(4)
Ag1−N1A	2.344(5)	Ag1−N5C	2.654(4)
Complex **2**			
Ag1−N1	2.217(7)	Ag2−N12	2.458(7)
Ag1−N7	2.351(6)	Ag2−N13	2.251(8)
Ag1−N5A	2.340(8)	Ag2−N18A	2.210(6)

Symmetry transformations used to generate equivalent atoms: For **1a**: A $-x, -y, -z$; B $x + 1, y, z$. C $-x + 1, -y, -z + 1$; D $x, -y + 0.5, z - 0.5$. For **1b**: A $-x - 0.5, -y, z + 0.5$; B $x - 1, y, z$.

For **1c**: A $-x + 1, y - 0.5, -z + 0.5$; B $-x + 2, y - 0.5, -z + 0.5$; C $-x + 1.5, -y, z - 0.5$. For **2**: A $x, y + 1, z$; B $x, y - 1, z$; C $-x + 2, y - 0.5, -z + 2$; D $-x + 2, y + 0.5, -z + 2$.

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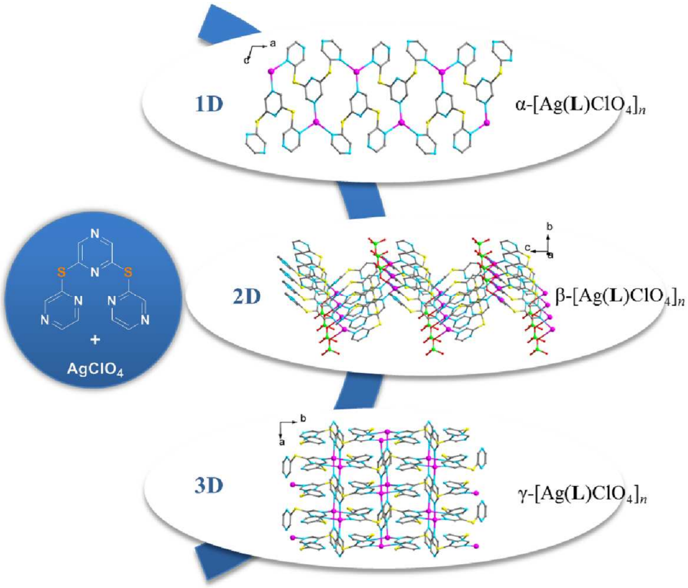

Three silver(I) supramolecular coordination isomers that display different dimensionalities and one homologue are derived from the conformationally flexible multidentate ligand 2,6-bis(pyrazin-2-ylthio)pyrazine (**L**).