#### Polyhedron 52 (2013) 122-127

Contents lists available at SciVerse ScienceDirect

# Polyhedron

journal homepage: www.elsevier.com/locate/poly

# Influence of anion on the network structure of one dimensional silver(I) coordination polymers of dicompartmental *N*,*N*-donor ligands

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#### ARTICLE INFO

Article history: Available online 5 November 2012

Dedicated to Professor Alfred Werner on the 100th Anniversary of his Nobel Prize in Chemistry in 1913.

Keywords: Silver Coordination polymer Nitrogen-donor ligand Solid-state structure Ligand conformer

#### ABSTRACT

Three one-dimensional silver(I) coordination polymers  $\{[AgL^1]NO_3\}_n$  (1),  $\{[AgL^2]ClO_4\}_n$  (2) and  $\{[AgL^2]NO_3\}_n$  (2a), where L<sup>1</sup> (pyridin-2-ylmethylene-(4-{[(pyridin-2-ylmethylene)-amino]-methyl}benzyl)-amine) is a dicompartmental iminopyridine ligand derived from the Schiff-base condensation of  $\alpha, \alpha'$ -diamino-*p*-xylene and pyridine-2-carboxaldehyde and L<sup>2</sup> (N-(4-((methyl(pyridin-2-ylmethyl)) amino)methyl)benzyl)-*N*-methyl(pyridin-2-yl)methanamine) is the reduced *N*-methyl derivative of L<sup>1</sup>, have been isolated from the reaction of ligands with various silver salts. Six different conformations of L<sup>1</sup> are known that give rise to different network structures for { $[AgL^1]ClO_4\}_n$ . X-ray single crystal structure of polymer 1-5H<sub>2</sub>O reveals that the asymmetric unit contains five water molecules that form a twodimensional hydrogen bonding network with nitrate counter anion. A new conformer of L<sup>1</sup> is observed in the polymeric structure of 1-5H<sub>2</sub>O. Coordination polymers **2** and **2a**, both made of  $[AgL^2]^+$  repeating unit, contains different conformers of L<sup>2</sup>. As a result, different polymeric structures are obtained for **2** and **2a**. The effect of counterion on the ligand conformation and subsequently on the polymeric structure is reported.

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# 1. Introduction

Since the development of Werner's Coordination theory, transition metal coordination complexes have found immense applications in chemistry, biology, material science and technology. The polymeric assemblies of transition metal ions and organic ligands have attracted considerable interests in coordination polymer chemistry [1-4]. The polymeric materials have potential applications in magnetic, electrical, optical, photophysical, host-guest chemistry and catalysis [2,5-10]. Versatile coordination geometries of transition metal ions give rise to a variety of polymeric architectures [1]. The formation of structurally diverse polymeric structures also depends on the geometry of ligands, solvents, counterions and reaction/crystallization conditions [11-17]. In addition, weak non-covalent interactions stabilize the polymeric network structure [18]. To achieve the desired properties of polymeric materials, it is necessary to have control on these parameters in order to isolate polymers with predictable structures and dimensions. This is a challenging job which needs an in-depth and systematic study. Moreover, coordination polymers derived from a flexible ligand exhibit supramolecular isomerism due to the presence of different conformations of the ligand during the selfassembly process [19-23]. The nature of the counter-anion and solvent of crystallization affect the conformation of such flexible ligand by various supramolecular interactions. Supramolecular isomerism with flexible ligands, 1,2-bis(4-pyridyl)ethane and 1,2-bis(4-pyridinecarboxamido)ethane has been well documented in the literature [24,25]. Furthermore flexible ligands based on aromatic spacers linked to thioetherpyridine unit results in multiple supramolecular structures [26–29].

We have recently reported the synthesis and characterization of structurally diverse silver(I) coordination polymers (general formula: { $[AgL^1]ClO_4\}_n$ ) derived from a conformationally flexible dicompartmental Schiff base ligand L<sup>1</sup> (Scheme 1) containing *p*-xylyl spacer between the two binding domains [30]. Two conformational supramolecular isomers have been isolated that differ in orientation of the flexible spacer in the coordination polymeric structures. Both *gauche* and *anti* conformations of the ligand were observed and six different conformers of the flexible ligand have been shown to stabilize in the solid-state structures of three coordination polymers [30]. The nature of the solvent has been shown to affect the topology of coordination polymeric structures.

As a continuation of our ongoing research on the coordination polymers of conformationally flexible ligands, we have isolated a family of silver(I) coordination polymers from different silver(I) salts. It is expected that the interaction between solvent and different counterions would lead to different conformations of the ligand. We have earlier shown that the reduction and subsequent *N*-methylation of iminopyridine groups in Schiff-base ligands





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 ${[AgL^2]NO_3}_n(2a)$ 

Scheme 1. Synthesis of silver(I) complexes.

resulted in a greater flexibility of the dinucleating ligands [31]. We have also tested the effect of *N*-methylation of  $L^1$  on the structure of coordination polymers.

We report herein the syntheses and characterization of silver(I) coordination polymers  $\{[AgL^1]X\}_n$  (X = NO<sub>3</sub>, **1**) and  $\{[AgL^2]X\}_n$  (X = ClO<sub>4</sub>, **2**; X = NO<sub>3</sub>, **2a**). We also report the solid-state structures of three coordination polymers **1**·5**H**<sub>2</sub>**O**, **2** and **2a**. The effects of the counter-anion and of *N*-methylation of L<sup>1</sup> on the topologies of silver(I) coordination polymers are discussed.

#### 2. Experimental

#### 2.1. Chemicals

Chemicals purchased from commercial sources were used for the synthesis of ligands and complexes. Solvents were distilled and dried prior to use. Although no problem was encountered during the synthesis of the complexes, perchlorate salts are potentially explosive and should be handled with care! [32]. Ligand L<sup>1</sup> (pyridin-2-ylmethyl-ene-(4-{[(pyridin-2-ylmethylene)-amino]-methyl}-benzyl)-amine) was synthesized according to the reported procedure [30]. The silver(I) complexes were synthesized and stored under dark.

#### 2.2. Syntheses

# 2.2.1. Synthesis of N-(4-((methyl(pyridin-2-ylmethyl)amino)methyl)benzyl)-N-methyl(pyridin-2-yl)methanamine (L<sup>2</sup>)

L<sup>2</sup> was prepared by reductive amination followed by *N*-methylation of ligand L<sup>1</sup> (1.58 g, 5 mmol) according to reported procedure [31]. The compound was isolated as a yellow liquid. Yield: 80% (1.4 g). IR (KBr, cm<sup>-1</sup>): 3304(br), 3167(br), 2920(m), 1697(m), 1589(m), 1470(m), 1433(m), 1281(m), 1234(s), 1090(s), 1036(m), 932(s). ESI-MS (positive ion mode, CH<sub>3</sub>CN): *m/z* = 347.08 (100%, [L<sup>1</sup> + H]<sup>+</sup>). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): *δ*, ppm: 8.50 (d, 2H, *J* = 4.5 Hz), 7.65 (t, 2H, *J* = 7.5 Hz), 7.51 (d, 1 H), 7.33 (s, 4H) 7.27 (s, 1 H), 7.14 (t, 2H), 3.69 (s, 2H), 3.58 (s, 2H), 2.24 (s, 6H).

#### 2.2.2. { $[AgL^1]NO_3$ }<sub>n</sub> (**1**)

To the solution of L<sup>1</sup> (0.32 g, 1 mmol) in dry MeOH (~15 mL) was added an acetonitrile (2–3 mL) solution of anhydrous silver(I) nitrate (0.18 g, 1 mmol). The light yellow solid was separated slowly upon stirring for 12 h at room temperature. The solid was isolated by filtration and dried in air. Single crystals were grown from the solvent mixture of acetonitrile and methanol. Yield: 62% (0.26 g). *Anal.* Calc. for  $C_{20}H_{18}AgN_5O_3$  (484.26 g/mol): C, 49.60; H, 3.75; N, 14.46. Found: C, 49.5; H, 3.7; N, 14.6%. IR (KBr, cm<sup>-1</sup>):

3460(br), 2924(m), 2852(m), 1645(s), 1589(s), 1437(m), 1383(m), 1365(s), 1296(m), 845(s), 779(s). ESI-MS (positive ion mode, CH<sub>3</sub>CN): m/z = 421.15 (100%,  $[L^1 + Ag]^+$ ). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ , ppm: 8.78 (s, 2H), 8.53 (d, 2H, *J* = 4.5 Hz), 8.14 (m, 2H), 7.93 (d, 2H, *J* = 7.5 Hz), 7.69 (m, 2H), 6.98 (s, 4H), 4.75 (s, 4H).

# 2.2.3. { $[AgL^2]ClO_4$ }<sub>n</sub> (**2**)

To the solution of L<sup>2</sup> (0.35 g, 1 mmol) in dry MeOH (~15 mL) was added anhydrous silver(I) perchlorate (0.20 g, 1 mmol). The light yellow solid was isolated by filtration after 12 h stirring at room temperature. Single crystals suitable for X-ray diffraction were obtained after 5 days from acetonitrile solution of the complex. Yield: 68% (0.55 g). *Anal.* Calc. for C<sub>22</sub>H<sub>26</sub>AgClN<sub>4</sub>O<sub>4</sub> (553.79 g/mol): C, 47.71; H, 4.73; N, 10.12. Found: C, 47.3; H, 4.7; N, 10.2%. IR (KBr, cm<sup>-1</sup>): 3470(br), 2924(m), 2848(m), 1743(m), 1593(s), 1437(m), 1365(m), 1144, 1117, 1088(s), 874(m), 769(s). ESI-MS (positive ion mode, CH<sub>3</sub>CN): *m/z* = 346.85 (60%,  $[L^2 + H]^*$ ), 453.63 (100%,  $[L^2 + Ag]^*$ ). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>):  $\delta$ , ppm: 8.59 (d, 2H, *J* = 4.5), 7.90 (t, 2H, *J* = 7.5 Hz), 7.41 (t, 2H, *J* = 6.0 Hz), 7.13 (S, 4H), 3.84 (s, 4H), 3.67 (s, 4H), 2.05(s, 6H).

### 2.2.4. { $[AgL^2]NO_3$ }<sub>n</sub> (**2a**)

Complex **2a** was synthesized using ligand L<sup>2</sup> (1 mmol) according to the procedure described for **1**. Single crystals of **2a** were grown from a solvent mixture of acetonitrile and methanol. Yield: 52% (0.29 g). *Anal.* Calc. for  $C_{22}H_{26}AgN_5O_3$  (516.34 g/mol): C, 51.17; H, 5.08; N, 13.56. Found: C, 51.1; H, 5.3; N, 13.5%. IR (KBr, cm<sup>-1</sup>): 3441(br), 3053(m), 2845(m), 1741(m), 1599(s), 1570(m), 1443(s), 1381(s), 1364(s), 1333(s), 1306(m), 1244(s), 1130(m), 1102(m), 833(s), 772(s). ESI-MS (positive ion mode, CH<sub>3</sub>CN): *m/z* = 455.06 (100%, [L<sup>2</sup> + Ag]<sup>+</sup>).

#### 2.3. Physical methods

Fourier transform infrared spectroscopy on KBr pellets was performed on a Shimadzu FT-IR 8400S instrument. Elemental analyses

Table 1Crystallographic data for 1.5H2O, 2 and 2a.

Parameters	1.5H <sub>2</sub> O	2	2a
Empirical formula Formula weight	$\begin{array}{l} C_{40}H_{36}Ag_2N_{10}O_{11}\\ 1048.53 \end{array}$	C <sub>22</sub> H <sub>26</sub> AgClN <sub>4</sub> O <sub>4</sub> 553.79	C <sub>22</sub> H <sub>26</sub> AgN <sub>5</sub> O <sub>3</sub> 516.35
Crystal system	orthorhombic	tetragonal	orthorhombic
Space group	Fddd	I-42d	Pbca
Unit cell dimensions			
a (Å)	17.263(3)	14.3358(7)	12.526(5)
b (Å)	22.510(4)	14.3358(7)	15.388(6)
c (Å)	45.316(8)	27.646(3)	23.192(9)
α (°)	90.00	90.00	90.00
β (°)	90.00	90.00	90.00
γ (°)	90.00	90.00	90.00
Volume (Å <sup>3</sup> )	17609(5)	5681.6(7)	4470(3)
Ζ	16	8	8
$D_{calc}$ (Mg/m <sup>3</sup> )	1.582	1.295	1.534
$\mu ({\rm mm}^{-1})$	0.959	0.833	0.935
F(000)	8448	2256	2112
$\theta$ Range data	1.55-21.99	1.60-23.47	1.76-21.78
collection (°)			
Reflections collected	30401	22242	28898
Reflections unique	2701	2098	2657
R <sub>int</sub>	0.0420	0.0614	0.0830
Data $(I > 2\sigma(I)$	1927	1637	2002
Parameters refined	287	144	282
Goodness-of-fit on F <sup>2</sup>	0.972	1.138	0.845
$R_1 \left[ I > 2\sigma(I) \right]$	0.0339	0.0588	0.0338
wR <sub>2</sub>	0.1141	0.1771	0.1013
Residuals (e Å <sup>-3</sup> )	-0.448, 0.221	-0.894, 0.376	-0.450, 0.436

were performed on a Perkin Elmer 2400 series II CHN analyzer. Electro-spray ionization mass spectra were recorded with a Waters QTOF Micro YA263. <sup>1</sup>H NMR spectra were measured at room temperature using Bruker DPX-500 spectrometer.

# 2.3.1. X-ray crystallographic data collection and refinement of the structures

Crystallographic data for **1**-5**H**<sub>2</sub>**O**, **2** and **2a** are given in Table 1. Diffraction data were collected at 120(2) K on a Bruker Smart APEX II (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å). Cell refinement, indexing and scaling of the data set were carried out using the Apex2 v2.1-0 software [33]. The structures were solved by direct methods and subsequent Fourier analyses and refined by the full-matrix leastsquares method based on  $F^2$  with all observed reflections [34]. In all the complexes the hydrogen atoms were fixed. The hydrogen atoms of water molecules in **1**-5**H**<sub>2</sub>**O** were not assigned. Oxygen atoms of the perchlorate anion in **2** were found to be disordered. All the non hydrogen atoms were refined anisotropically except the disordered perchlorate anion of **2**. The routine SQUEEZE was applied to intensities data of isomer **2** to take into account the disordered solvent molecules [35].

# 3. Results and discussion

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# 3.1. Syntheses and characterization

The silver(I) complexes were synthesized by mixing equimolar amounts of ligands and silver(I) salts in methanol (Scheme 1). All the complexes were characterized by several spectroscopic and



**Fig. 1.** The cationic repeating unit in the polymeric chain of **1**. The counterions are omitted for clarity. Symmetry code: (') 1/4 - x, 5/4 - y, *z*.

Selected bond lengths (Å) and angles (°) for <b>1.5H<sub>2</sub>O</b> .			
Ag(1)-N(1)	2.353(4)	Ag(1)-N(2)	2.302(4)
Ag(2)-N(3)	2.327(4)	Ag(2)-N(4)	2.336(4)
N(1)-Ag(1)-N(1)	136.83(17)	N(2)-Ag(1)-N(1)	129.44(13
N(2)-Ag(1)-N(1)	72.95(14)	N(2)-Ag(1)-N(2)	124.58(18
N(3)-Ag(2)-N(3)	124.01(19)	N(3)-Ag(2)-N(4)	72.47(15)
N(3)-Ag(2)-N(4)	129.78(13)	N(4)-Ag(2)-N(4)	137.7(2)

analytical techniques. IR spectra of the complexes display the characteristic bands due to the counterions in addition to the bands expected from the coordinated ligands. <sup>1</sup>H NMR spectral data of the complexes exhibit proton resonances slightly different from that of the free ligands, indicating the presence of equilibrium between the ligand and silver salt in solution. ESI-MS and elemental analysis of the complexes suggest the 1:1 metal-ligand composition with respective counterions.

#### 3.2. X-ray structures

To understand the structure of the complexes in solid-state, efforts were made to grow the single-crystals of the complexes. Single-crystals of  $1.5H_2O$ , **2** and **2a** were isolated for X-ray diffraction. The silver ions in all the complexes exhibit four-coordinate distorted tetrahedral coordination geometry with two nitrogens either from amine or imine moiety and two pyridine nitrogen donors from the ligands.

#### 3.2.1. Crystal structure of 1.5H<sub>2</sub>O

Single crystals of  $1.5H_2O$  suitable for X-ray diffraction were isolated from a solvent mixture of acetonitrile and methanol and the complex crystallized in an orthorhombic *Fddd* space group. X-ray structure of  $1.5H_2O$  reveals the presence of two silver ions, two Schiff-base ligands (L<sup>1</sup>), two nitrates and five water molecules in the asymmetric unit. The cationic part consisting of the [AgL<sup>1</sup>]<sup>+</sup> unit is repeated to form a one-dimensional coordination polymer (Fig. 1). In each of the repeating unit, the average Ag–N<sub>imine</sub> and Ag–N<sub>pyridine</sub> distances (Table 2) are found to be 2.340(4) Å and 2.319(4) Å, respectively, which are in good agreement with the previously reported silver(I) complexes of L<sup>1</sup> with perchlorate counterion.[30]

The polymeric chain in **1** elongates along the crystallographic *ab* plane (Fig. 2) where the ligand in the repeating unit adopts an *anti* conformations with the torsion angles across the phenyl spacer N2–C7…C14–N3 being 140.68°. Although the ligand adopts an *anti* conformation as observed in different supramolecular isomers of  $\{[AgL^1]ClO_4\}_n$  [30], a new *anti* conformation of L<sup>1</sup> makes the polymeric structure of **1** different from the perchlorate complex. Due to this particular conformation of the ligand, the silver ions are disposed along two parallel vectors resulting in the formation of a triangular wave polymeric chain with the distance between the two adjacent silver ions of 7.315 Å and the Ag–Ag–Ag angle of 151.6° (Fig. 2). Weak  $\pi$ … $\pi$  interactions are observed in the polymeric chains between the phenyl ring of *p*-xylyl spacer and pyridine rings with the distances of 4.54 and 4.53 Å (Fig. 2a).

Each of the asymmetric units of **1** consists of five water molecules and two counter-anions along with two repeating units. Water molecules and nitrate ions are assembled through hydrogen bonding in the solid-state and forms two-dimensional network (Fig. 3a) resulting in a planar hexameric water cluster (Fig. 3b). In this particular network each water cluster is surrounded by four nitrate anions. The O…O distances between the water molecules in the cluster are in a range of 2.47–2.73 Å whereas other O…O



Fig. 2. (a) One-dimensional polymeric chain of 1 and (b) view along the crystallographic plane ab.



Fig. 3. (a) Two-dimensional hydrogen-bonded network and (b) hexameric water cluster consisting of water molecules and nitrate anions.



Fig. 4. Propagation of the coordination polymer  $1.5H_2O$  through the channels formed by hydrogen-bonded network involving nitrate counterions and water molecules.

distances are quite longer and in a range of 3.01–3.03 Å. The hexameric water cluster is proposed to be the smallest unit in bulk water [36]. Hexameric water clusters with different conformations including planar water hexamer in the lattice of coordination compounds have been reported in literature [37–49].

A two-dimensional hydrogen-bonded network between the solvent molecules and anions creates void channels through which the polymeric chains are propagated (Fig. 4).

It is important to mention that six different conformations of the flexible ligand  $L^1$  have been found in the solid-state structure of the silver(I) complex {[AgL<sup>1</sup>]ClO<sub>4</sub>}<sub>n</sub> depending upon the crystallization technique and the solvent of crystallization [30]. The solidstate packing of **1.5H<sub>2</sub>O** leads to a new conformer of  $L^1$  with the torsion angle of 140.68° (Fig. 5). This is an outcome of the effect of interaction between the counter-anion (nitrate) and water molecules present in the solvent used for crystallization. Including this conformation, a total number of seven conformations are now known for the flexible Schiff-base ligand.

# 3.2.2. Crystal structure of **2**

Complex  $\{[AgL^2]ClO_4\}_n$  (**2**) was isolated to see the effect of the reduction of imine moiety and subsequent *N*-methylation on L<sup>1</sup>. Single-crystals of **2** were isolated from an acetonitrile solution of the complex and were crystallized in tetragonal *I*-42*d* space group.



**Fig. 5.** Conformations of L<sup>1</sup> observed in the solid-state structures of silver(1) coordination polymers  $\{[AgL^1]CIO_4\}_n$  [30] and  $\{[AgL^1]NO_3\}_n$ . The torsion angles across the phenyl ring (N-C···C-N) for each conformation is provided at the bottom.



**Fig. 6.** Repeating unit of the polymeric chain in **2**. The counter-anions are omitted for clarity. Symmetry codes: (') 1 - x, 1 - y, z; (") 1 - x, -1/2 + y, 1/4 - z.

Table 3	
Selected bond lengths (Å) and angles (°) for <b>2</b> .	

Ag(1)-N(1)	2.299(6)	Ag(1)-N(2)	2.391(5)
N(1)-Ag(1)-N(1')	117.5(3)	N(2)-Ag(1)-N(1)	73.7(2)
N(1')-Ag(1)-N(2)	140.0(2)	N(2)-Ag(1)-N(2')	124.2(3)

Symmetry code: (') 1 - x, 1 - y, z.

The single-crystal X-ray structure of **2** (Fig. 6) displays a onedimensional polymeric chain with one ligand ( $L^2$ ), one silver(I) ion and a perchlorate anion as the repeating unit. The Ag–N distances and N–Ag–N angles (Table 3) are comparable with **1** and with other reported silver(I) complexes [30,31,50,51].



Fig. 7. Propagation of one-dimensional polymeric chain in 2 along crystallographic b axis.



**Fig. 8.** Repeating unit of the polymeric chain of **2a**. The counterions are omitted for clarity. Symmetry code: (') -x, 2 - y, -z; ('') -x, 1 - y, -z.

Table 4	
Selected bond lengths (Å) and angles (°) for <b>2a</b> .	

Ag(1)-N(1)	2.313(4)	Ag(1)-N(2)	2.436(4)
Ag(1)-N(3)	2.549(4)	Ag(1)-N(4)	2.260(5)
N(4)-Ag(1)-N(1)	144.84(13)	N(4)-Ag(1)-N(2)	142.36(13)
N(1)-Ag(1)-N(2)	71.89(14)	N(4)-Ag(1)-N(3)	71.52(13)
N(1)-Ag(1)-N(3)	106.15(13)	N(2)-Ag(1)-N(3)	113.56(13)

The  $[AgL^2]^+$  unit in **2** is repeated along the crystallographic axis *b* (Fig. 7) in a zigzag fashion. The metal ions in the polymeric chain are positioned along two parallel vectors forming a triangular wave where two adjacent silver atoms are separated by 7.233 Å with the Ag–Ag–Ag angle of 164.58°. Ligand L<sup>2</sup> in the polymer chain adopts an *anti* conformation with the torsion angle across the phenyl spacer N2–C8…C8′–N2′ of 146.44°. The coordination of tertiary amine nitrogen to the metal center makes the amine nitrogen chiral. All the amine nitrogens have *R* configuration and similar configuration of all the silver centers results in the formation of a chiral, isotactic polymer. In this particular arrangement of the polymer, weak  $\pi$ … $\pi$  interactions among the spacer phenyl ring



**Fig. 10.** Two different conformations of L<sup>2</sup> along with their torsion angles across *p*-xylyl spacer observed in the solid-state structures of **2** and **2a**.

and pyridine ring are observed with the centroid-to-centroid distance of 5.43 Å.

# 3.2.3. Crystal structure of 2a

Single crystals of  $\{[AgL^2]NO_3\}_n$  (**2a**) were grown from a solvent mixture of acetonitrile and methanol. The complex crystallized in orthorhombic *Pbca* space group. X-ray structural analysis of **2a** 



Fig. 9. Propagation of one-dimensional polymeric chain in 2a. (b) View along crystallographic b axis.

(Fig. 8) establishes the complex to be a coordination polymer consisting of  $[AgL^2]^+$  repeating unit and perchlorate counterion. In this molecule, the average Ag-N<sub>amine</sub> distance is significantly longer than the average Ag-N<sub>pyridine</sub> distance (Table 4). An anti conformation of the ligand is present in the polymeric chain with the torsion angle across the phenyl spacer being 180.00°. The effect of nitrate on the polymeric structure is evident in this complex compared to that in the perchlorate complex 2.

The polymeric chain of **2a** is propagated along crystallographic b axis (Fig. 9) in a zigzag fashion where the metal ions are aligned along two parallel vectors forming an asymmetrical triangular wave. The distances between two adjacent silver ions connected by  $L^2$  are 8.33 and 12.74 Å, respectively. In spite of the presence of a single anti isomer, the asymmetry in distance between the silver centers arises due to a trans arrangement between the two binding sites of the flexible dicompartmental ligand. It is important to note that the tertiary amine nitrogens of the ligand exhibit RSSR type configuration along the polymer chain.

It is clear from the above discussion that in spite of the presence of repeating units having same metal-ligand compositions, the polymeric structure of 2 and 2a are different. Two different polymeric networks result from the different conformations adopted by the flexible ligand (Fig. 10). Moreover, different configuration of amine nitrogens in L<sup>2</sup> upon binding with silver in two complexes gives rise to different polymeric architectures.

#### 4. Conclusions

Three one-dimensional silver(I) coordination polymers of bis(bidentate) nitrogen donor ligands  $L^1$  and  $L^2$  have been prepared and structurally characterized by X-ray single-crystal diffraction. Solid-state structure of **1**-5H<sub>2</sub>O reveals a new anti conformer of  $L^1$  in the polymeric network. A two-dimensional hydrogen bonding network involving water and nitrate in 1.5H<sub>2</sub>O affect the conformation of L<sup>1</sup>. Two polymeric complexes 2 and 2a are isolated in the reaction of ligand L<sup>2</sup> with silver(I) perchlorate and silver nitrate, respectively. Different *anti* conformers of ligand  $L^2$  in **2** and 2a result in different polymeric structures. The results demonstrate the effect of the counter-anion on the ligand flexibility and on the resulting solid-state structures of silver(I) coordination polymers.

#### Acknowledgments

Financial support from the Department of Science and Technology, Government of India is gratefully acknowledged. Single-crystal diffraction data were collected at the DST-funded National Single Crystal Diffractometer Facility at the Department of Inorganic Chemistry, IACS. B.C. acknowledges the Council of Scientific and Industrial Research (CSIR), India for a fellowship.

#### **Appendix A. Supplementary material**

CCDC 876426-876428 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

#### References

- [1] W.L. Leong, J.J. Vittal, Chem. Rev. 111 (2011) 688.
- [2] C. Janiak, Dalton Trans. (2003) 2781.
- S.R. Batten, S.M. Nevile, D.R. Turner, Coordination Polymers: Design, Analysis [3] and Application, The Royal Society of Chemistry, Cambridge, UK, 2009 [4] A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga,
- N.V. Zyk, M. Schröder, Coord. Chem. Rev. 222 (2001) 155. [5] YY Karabach MEC Guedes da Silva MN Kopylovich B Gil-Hernandez I
- Sanchiz, A.M. Kirillov, A.J.L. Pombeiro, Inorg. Chem. 49 (2010) 11096. [6] M. Mitsumi, K. Kitamura, A. Morinaga, Y. Ozawa, M. Kobavashi, K. Toriumi, Y.
- Iso, H. Kitagawa, T. Mitani, Angew. Chem., Int. Ed. 41 (2002) 2767. [7]
- S. Shimomura, M. Higuchi, R. Matsuda, K. Yoneda, Y. Hijikata, Y. Kubota, Y. Mita, J. Kim, M. Takata, S. Kitagawa, Nat. Chem. 2 (2010) 633.
- K. Hirai, H. Uehara, S. Kitagawa, S. Furukawa, Dalton Trans. 41 (2012) 3924.
- [9] P. Phuengphai, S. Youngme, P. Gamez, J. Reedijk, Dalton Trans. 39 (2010) 7936.
- [10] F.L. Yang, J. Tao, R.B. Huang, L.S. Zheng, Inorg. Chem. 50 (2011) 911.
- [11] K. Chainok, S.M. Neville, C.M. Forsyth, W.J. Gee, K.S. Murray, S.R. Batten,
- CrystEngComm 14 (2012) 3717 [12] C. Desmarets, I. Azcarate, G. Gontard, H. Amouri, Eur. J. Inorg. Chem. (2011) 4558.
- [13] M.O. Awaleh, A. Badia, F. Brisse, Cryst, Growth Des. 5 (2005) 1897.
- [14] X.-H. Bu, W. Chen, W.-F. Hou, M. Du, R.-H. Zhang, F. Brisse, Inorg. Chem. 41 (2002) 3477.
- M. Hong, W. Su, R. Cao, M. Fujita, J. Lu, Chem. Eur. J. 6 (2000) 427.
  C. Janiak, L. Uehlin, H.-P. Wu, P. Klüfers, H. Piotrowski, T.G. Scharmann, J.
- Chem. Soc., Dalton Trans. (1999) 3121. [17] H.-P. Wu, C. Janiak, G. Rheinwald, H. Lang, J. Chem. Soc., Dalton Trans, (1999) 183
- [18] C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885.
- [19] B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629.
- [20] M.J. Zaworotko, Chem. Commun. (2001) 1.
- [21] S.A. Bourne, J. Lu, B. Moulton, M.J. Zaworotko, Chem. Commun. (2001) 861.
- [22] J.-P. Zhang, X.-C. Huang, X.-M. Chen, Chem. Soc. Rev. 38 (2009) 2385.
- [23] C.B. Aakeröy, N.R. Champness, C. Janiak, CrystEngComm 12 (2010) 22.
- [24] T.L. Hennigar, D.C. MacQuarrie, P. Losier, R.D. Rogers, M.J. Zaworotko, Angew. Chem., Int. Ed. 36 (1997) 972.
- M. Sarkar, K. Biradha, Cryst. Growth Des. 7 (2007) 1318. [25]
- [26] L.R. Hanton, K. Lee, J. Chem. Soc., Dalton Trans. (2000) 1161.
- [27] P.L. Caradoc-Davies, L.R. Hanton, Chem. Commun. (2001) 1098.
- [28] P.L. Caradoc-Davies, D.H. Gregory, L.R. Hanton, J.M. Turnbull, J. Chem. Soc., Dalton Trans. (2002) 1574.
- [29] D.B. Cordes, A.S. Bailey, P.L. Caradoc-Davies, D.H. Gregory, L.R. Hanton, K. Lee, M.D. Spicer, Inorg. Chem. 44 (2005) 2544.
- [30] B. Chakraborty, P. Halder, T.K. Paine, Dalton Trans. 40 (2011) 3647.
- [31] P. Halder, E. Zangrando, T.K. Paine, Dalton Trans. (2009) 5386.
- [32] W.C. Wolsey, J. Chem. Educ. 50 (1973) A335.
- [33] APEX 2, 2.1-0 Ed., Bruker AXS Inc., Madison, WI, 2006.
- [34] G.M. Sheldrick, SHELX97 Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, 1998.
- [35] P. van der Sluis, A.L. Spek, Acta Crystallogr., Sect. A 46 (1990) 194.
- [36] R. Ludwig, Angew. Chem., Int. Ed. 40 (2001) 1808.
- [37] Y. Wang, L. Yi, X. Yang, B. Ding, P. Cheng, D.-Z. Liao, S.-P. Yan, Inorg. Chem. 45 (2006) 5822.
- [38] S.K. Ghosh, P.K. Bharadwaj, Inorg. Chem. 42 (2003) 8250.
- [39] R. Luna-García, B.M. Damián-Murillo, V. Barba, H. Höpfl, H.I. Beltrán, L.S. Zamudio-Rivera, Chem. Commun. (2005) 5527.
- [40] Y.-C. Liao, Y.-C. Jiang, S.-L. Wang, J. Am. Chem. Soc. 127 (2005) 12794.
- [41] J.N. Moorthy, R. Natarajan, P. Venugopalan, Angew. Chem., Int. Ed. 41 (2002) 3417
- [42] S.K. Ghosh, P.K. Bharadwaj, Angew. Chem., Int. Ed. 43 (2004) 3577.
- [43] U. Mukhopadhyay, I. Bernal, Cryst. Growth Des. 5 (2005) 1687.
- [44] B.-H. Ye, B.-B. Ding, Y.-Q. Weng, X.-M. Chen, Inorg. Chem. 43 (2004) 6866.
- [45] R. Custecean, C. Afloroaei, M. Vlassa, M. Polverejan, Angew. Chem., Int. Ed. 39 (2000) 3094.
- [46] Y.-P. Ren, L.-S. Long, B.-W. Mao, Y.-Z. Yuan, R.-B. Huang, L.-S. Zheng, Angew. Chem., Int. Ed. 42 (2003) 532.
- [47] F. Zhuge, B. Wu, J. Liang, J. Yang, Y. Liu, C. Jia, C. Janiak, N. Tang, X.-J. Yang, Inorg. Chem. 48 (2009) 10249.
- [48] B.-Q. Ma, H.-L. Sun, S. Gao, Eur. J. Inorg. Chem. (2005) 3902.
- [49] B. Chakraborty, T.K. Paine, Inorg. Chim. Acta 378 (2011) 231.
- [50] H.-C. Wu, P. Thanasekaran, C.-H. Tsai, J.-Y. Wu, S.-M. Huang, Y.-S. Wen, K.-L. Lu, Inorg. Chem. 45 (2006) 295.
- [51] F. Tuna, J. Hamblin, G. Clarkson, W. Errington, N.W. Alcock, M.J. Hannon, Chem. Eur. J. 8 (2002) 4957.