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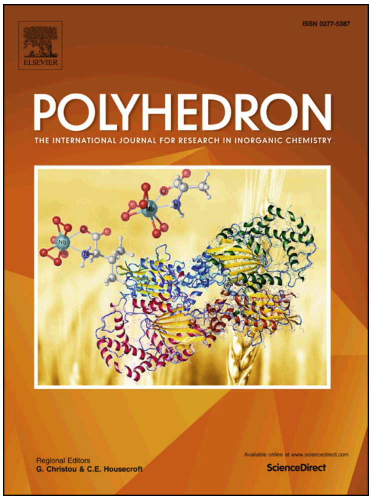

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Self-assembly of three cationic silver(I) coordination networks with flexible bis(pyrazoly)-based linkers

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Abstract

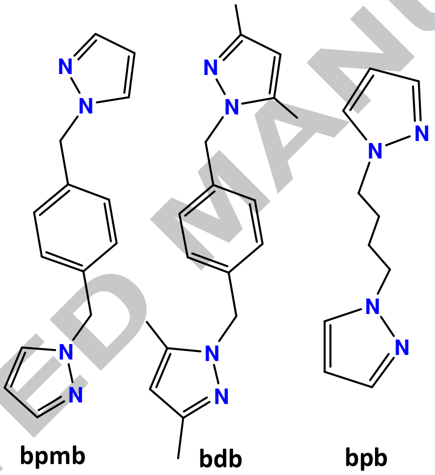
Three new cationic silver(I) coordination polymers, $\{[Ag(\mu\text{-bpmb})](SO_3CF_3)\}_n$ (**1**), $\{[Ag(\mu\text{-bdb})_{1.5}](SO_3CF_3)\}_n$ (**2**) and $\{[Ag(\mu\text{-bpb})_2](NO_3)\}_n$ (**3**), with flexible 1,4-bis[(pyrazolyl)methyl]benzene (bpmb), 1,4-bis[(3,5-dimethylpyrazolyl)methyl]benzene (bdb), and 1,4-bis(pyrazolyl)butane (bpb) have been prepared at room temperature by the solvent layering method. The three compounds were characterized by FT-IR spectroscopy, PXRD, elemental analyses and single-crystal X-ray diffraction. Compound **1** is a highly undulated polymeric 1D chain in which the silver ions adopt a linear geometry, coordinating two bpmb linkers. Compounds **2** and **3** are both 2D coordination polymers with their silver atoms being three and four coordinated, and resulting in **6^3-hcb** and **4^4-sql** underlying net topologies, respectively. The flexible bispyrazolyl ligands display various conformations in the solid state, causing the formation of different Ag...Ag separations in the polymeric structures.

Keywords: Silver(I), coordination polymer, flexible ligand, pyrazolyl ligand.

1. Introduction

The construction of coordination polymers (CPs) by the self-assembly of metal ions or metal clusters and organic linkers is an active research area. Such interest is not only due to the creation of a great variety of fascinating structures, from one-dimensional chains to two-dimensional sheets and three-dimensional networks, [1] but also to the wide range of applications of CPs, including gas storage (particularly hydrogen storage) and separation [2], catalysis [3], explosives [4], biomedicine, optical and electronic devices [5]. When rigid bridging ligands are involved in the self-assembly process, it is easier to design predictable networks with desired structures and appropriate properties, while using flexible ligands makes it difficult to design favored supramolecular architectures. However, the flexibility of the linkers usually generates greater structural diversity with possible unusual entanglements [6]. The self-assembly process in the presence of flexible linkers is influenced by a number of factors, including the nature of the solvent and counter ion, mole ratio of the reagents, coordination preference of the metal ion and geometry of the linker ligands [3f,7]. Non-covalent weak interactions, such as C-H hydrogen bonds, π···π stacking and C-H···π interactions, may also be expected to play a role in the assembly and dimensionality of the resulting structures [8].

Among variety of polymeric structures reported up until now, Ag(I) and Cu(I) ions are particularly well-suited cations for study, because they display a variety of coordination numbers and coordination geometries without crystal field stabilization energy preferences [9]. These CPs also exhibit outstanding luminescent properties and the silver(I) species exhibit well-known antibacterial activity [10]. In the structure of Ag(I) CPs, the silver(I) ion can associate in Ag···Ag interactions that can play a significant role in directing the assembly of the coordination networks. On the basis of our experiences on the design and synthesis of copper(I) and silver(I) coordination polymers [7d,e, 11], in this current work we explore the type of coordination polymers that can be formed by combining flexible bispyrazolyl ligands (scheme 1) with Ag(I) centers in the presence of triflate and nitrate ions. We report herein the synthesis and structural characterization of three new silver(I) coordination polymers and investigate the effect of the ligand geometry and weak non-covalent interactions on their structures and dimensionality. We hope that this work will assist in identifying factors that govern the structure of coordination polymers and thus provide a basis for the rational design of coordination polymers constructed from flexible bridging ligands.



Scheme 1. Structure of the bispyrazolyl linker ligands

2. Experimental

2.1. Materials and physical measurements

All experiments were carried out in air. The starting materials were purchased from commercial sources and used without further purification. The infrared spectra (4000-400 cm^{-1}) were recorded as KBr discs with a BOMEN MB102 FT-IR spectrometer. The elemental analyses for C, H and N were performed on a Costech-ECS 4010 CHNSO analyzer. X-ray powder diffraction patterns were recorded on a Philips X'Pert Pro diffractometer (Cu Kα radiation, λ = 1.54184 Å) in the 2θ range 5-50°. The simulated XRD powder patterns, based on single crystal data, were obtained using Mercury software [12].

2.2. Synthetic procedures

2.2.1. Preparation of the bpmb, bdb and bpb ligands: The ligands were prepared according to the published methods [13]. Typically, a mixture of pyrazole (1.36 g, 20 mmol) or 3,5-dimethyl-pyrazole (1.92 g, 20 mmol) and finely powdered potassium hydroxide (2.24 g, 40 mmol) in DMSO (12 mL) were vigorously stirred at 80 ºC for 2 h. Then, the corresponding dihalide, 1,4-bis(chloromethyl)benzene (1.64 g, 10 mmol) or 1,4-dichlorobutane (1.11 mL, 10 mmol), in DMSO (5 mL) was added dropwise to the slurry mixture. The mixture was stirred at 80 ºC until completion of the reaction (checked by TLC). The mixture was then cooled to room temperature and the vessel was moved to an ice bath. 250 mL of cooled water was poured into the reaction mixture and a precipitate formed immediately, which was collected by filtration, washed with water and dried under vacuum. In the case of bpb, as the product is a liquid, the reaction mixture was poured into water (250 mL) and extracted with chloroform (3 × 20 mL). The extract was washed with water (2 × 20 mL) and dried over calcium chloride. After evaporation of chloroform under vacuum, the product was isolated as a yellow oil.

2.2.2. Synthesis of $\{[Ag(\mu\text{-bpmb})](SO_3CF_3)\}_n$ (1)

A solution of bpmb (15 mg, 0.06 mmol) in 3 mL of acetone was gently layered on the top of a clear solution of $AgSO_3CF_3$ (10 mg, 0.04 mmol) in 3 mL of water in a test tube. The vessel was covered by aluminum foil and kept in a dark place. Colorless needle-shaped single crystals of **1** suitable for X-ray crystallography were obtained after 2 days. They were collected and dried in air. (0.015 g, 76% yield based on Ag). Anal. Calcd for $C_{15}H_{14}AgF_3N_4O_3S$: C 36.38, H 2.85, N 11.31; Found: C 36.51, H 2.90, N 11.12%.

2.2.3. Synthesis of $\{[Ag(\mu\text{-bdb})_{1.5}](SO_3CF_3)\}_n$ (2)

A solution of bdb (30 mg, 0.12 mmol) in 4 mL of acetone was gently layered on the top of a clear solution of $AgSO_3CF_3$ (15 mg, 0.06 mmol) in 4 mL of water in a test tube. The vessel was covered by aluminum foil and kept in a dark place. Colorless needle-shaped single crystals of **2** suitable for X-ray crystallography were obtained after a week. They were collected and dried in air. (41 mg, 81% yield based on Ag). Anal. Calcd for $C_{28}H_{33}AgF_3N_6O_3S$: C 48.15, H 4.76, N 12.03; Found: C 47.72, H 4.50, N 11.85%.

2.2.4. Synthesis of $\{[Ag(\mu\text{-bpb})_2](NO_3)\}_n$ (3)

A solution of bpb (0.11 g, 0.57 mmol) in 4 mL of EtOH was gently layered on the top of a clear solution of $AgNO_3$ (0.05 g, 0.29 mmol) in 4 mL of water in a test tube. The vessel was covered by aluminum foil and kept in a dark place. Colorless cubic single crystals of **3** suitable for X-ray crystallography were obtained after two weeks. They were collected and dried in air. (55 mg, 34% yield based on Ag). Anal. Calcd for $C_{20}H_{28}AgN_9O_3$: C 43.65, H 5.12, N 22.91; Found: C 43.60, H 5.12, N 23.43%.

2.3. Single crystal X-ray crystallographic studies:

X-ray data were collected on a Bruker Apex II diffractometer using MoKα radiation. The structures were solved using direct methods and refined using a full-matrix least squares procedure based on F^2 using all data [14]. Hydrogen atoms were placed at geometrically estimated positions. The high R value for compound **3** is intrinsically related to the high flexibility of the ligand. Different collection data were obtained from several crystals at room and low temperature without improving the final refinement beyond the one reported. Details relating to the crystals and the structural refinements are presented in Table 1. Full details of the crystal data and the structure refinements, in CIF format, are available as Supporting Information.

Table 1. Crystallographic data and structure refinement details for **1-3**.

Compound	**1**	**2**	**3**
Formula	$C_{15}H_{14}AgF_3N_4O_3S$	$C_{28}H_{33}Ag\ F_3N_6O_3S$	$C_{20}H_{28}AgN_9O_3$
Molecular weight	495.23	698.53	550.38
T (K)	293	293	293
Cryst syst	Triclinic	monoclinic	monoclinic
space group	P-1	P21/c	P2/c
a (Å)	9.2496(16)	15.623(5)	17.4440(3)
b (Å)	10.1206(17)	15.226(5)	8.4164(12)
c (Å)	11.698(2)	13.409(5)	33.155(5)
α (°)	68.602(2)	90	90
β (°)	74.582(3)	101.587(5)	104.594(2)
γ (°)	65.432(2)	90	90
V (Å^3)	918.8(3)	3124.7(18)	4709.5(13)
Z	2	4	8
Dcalcd (g cm^{-3})	1.790	1.485	1.553
Data collected	20332	731650	92315
Unique data (R_{int})	5293 (0.048)	10079 (0.037)	13192 (0.055)
data/restraints/params	5293/0/244	10079/0/379	13192/172/597
R1[$I > 2\sigma(I)$]	0.0420	0.0505	0.1003
wR$_2$ (all data)	0.0960	0.1479	0.2365

3. Results and discussion

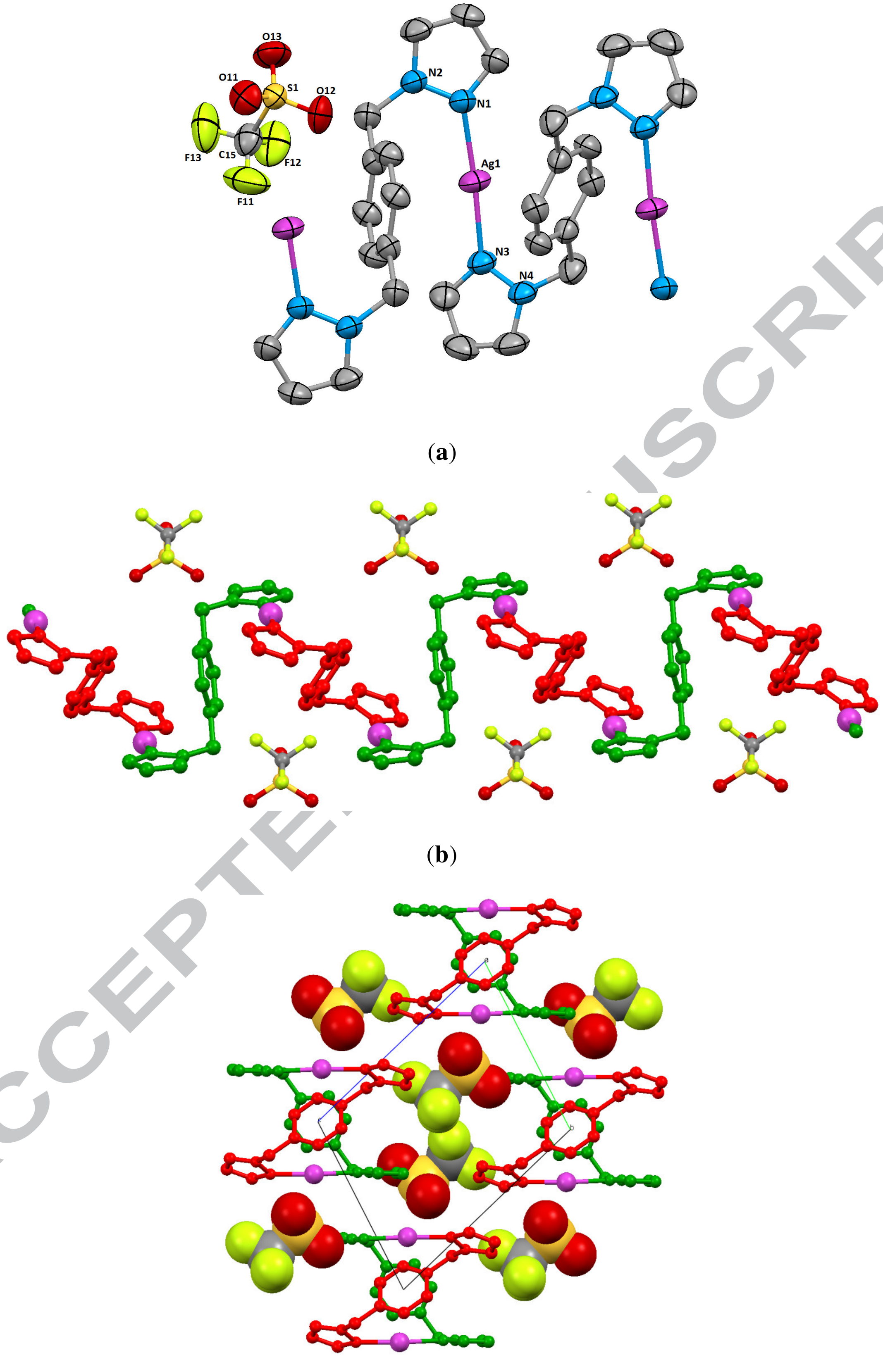
3.1. Synthesis of complexes 1-3.

The silver(I) coordination polymers were prepared at room temperature by the solvent layering method, reacting silver(I) triflate or nitrate salts with the bis(pyrazolyl) ligands. The solvent layering method is a simple and efficient strategy to obtain high quality single crystals of Ag(I) CPs. The complexes are almost stable towards air and moisture; they were characterized by elemental analyses, FT-IR spectroscopy, PXRD and single-crystal X-ray diffraction.

3.2. Description of the crystal structures

3.2.1. Crystal structure of {[Ag(μ-bpmb)](SO_3CF_3)}$_n$ (1)

Compound **1** crystallizes in the triclinic space group P-1 with *Z* = 2 (Table 1). The structure consists of square-wave-like cationic 1D polymeric chains and the uncoordinated triflate counteranion, $SO_3CF_3^-$ (Figure 1b). The asymmetric unit contain one silver atom, one triflate anion and two halves of two centro-symmetric ligands (Figure 1a). The Ag(I) centers are bound to the N atoms of two pyrazolyl groups from separate ligands, forming an almost linear AgN_2 geometry [Ag−N= 2.136(2) and 2.138(2) Å; N-Ag-N=175.37(13)°]. The bridging ligands are crystallographically independent and hence exhibit different (Ag)N…N(Ag) distances (7.79 and 7.96 Å for the green and red color linkers, respectively) and two different Ag···Ag separations of 7.25 and 6.61 Å along the chain. Usually, the metal•••metal separation should be longer than the linker length, however the *anti* conformation of the bpmb ligands are such as to bring the two coordination sides of the ligand into close proximity of each other and provide a shorter Ag···Ag distance. All the ligands are centrosymmetric, with centers of inversion located at the center of phenyl spacer rings. It follows that the mean planes of the pyrazolyl rings are parallel. The phenyl rings of both independent ligands are almost perpendicular to the corresponding pyrazolyl mean planes, 83.9° (N3N4) and 81.2° (N1N2). All the chains within the crystal are parallel and extend along the crystallographic *a* axis. The structure is arranged in a manner that the phenyl spacers are stacked along the *a* axis (Figure 1c).



(**a**)

(**b**)

(**c**)

Figure 1. The structure of {[Ag(μ-bpmb)](SO$_3$CF$_3$)}$_n$ (**1**). (a) Part of the infinite chain with the numbering scheme; centers of inversion are located at the centre of the phenyl spacer rings (b) Ball and stick representation of the extended polymeric chain, showing two different conformations for the bpmb linkers (c) Packing of the chains along the *a* axis; the triflate anions are located between the chains without any interaction with the silver(I) ions.

The triflate anions are located between the cationic [Ag(μ-bpmb)]^+_n chains (Figure 1c) and show only weak C−H···O hydrogen bonds between its oxygen atoms and the neighboring hydrogen atoms of pyrazolyl or methylene groups. Details of the hydrogen bonding geometry are given in Figure S1 and Table S2 [Supporting information]. The main non-covalent interactions present in **1** are two types of inter-chain π···π stacking involving crystallographically equivalent pyrazolyl rings of adjacent chains. These are characterized by centroid···centroid distances of 3.567(3) and 3.870(2) Å for the perfectly parallel N3N4 and N1N2 pyrazolyl groups, respectively [15]. Taking into account such π···π weak interactions, the 1D coordination motifs extend to a 3D supramolecular architecture.

Curiously, looking in the literature we found a crystal structure that shows similarities with compound **1** which is worth commenting on. {[Ag(μ-L)](ClO$_4$)}$_n$ L= 1,4-bis(imidazol-1-ylmethyl)naphthalene with CSD refcode HEXLUS [16], is a silver 1D chain very similar to **1**. Despite the differences in the nature of the ligands and counteranions, the two structures show very similar crystallographic parameters and structural features. Both compounds show square wave-like chains that are connected to each other through π···π interactions. However, in HEXLUS there are naphthalene instead of phenyl spacers, which are oriented almost perpendicular to the running direction of the [0 1 -1] chains, that are involved in inter-chain π···π stacking, while in **1** the terminal five membered rings are involved in the inter-chains π···π interactions.

3.2.2. Crystal structure of $\{[Ag(\mu\text{-bdb})_{1.5}](SO_3CF_3)\}_n$ (2)

Compound **2** is a two-dimensional structure that crystallizes in the monoclinic space group P21/c with Z= 4 (Table 1). The asymmetric unit consists of one silver(I) ion, one and a half bdb ligands and an uncoordinated triflate ion as a counter anion (Figure 2). The silver(I) ions are coordinated by three N atoms of μ-bdb linkers in a distorted trigonal planar, TP, geometry with angles between 101.00(8) and 142.44(9)° (Table S1). Deviation from the ideal TP geometry is probably due to the large steric hindrance induced by the 3,5-dimethylpyrazole rings of the μ-bdb ligands. The Ag-N distances are in the range 2.215(2)-2.362(2) Å. Due to the coordination of the bdb linkers to the silver centres, 66-membered cationic $[Ag_6(\mu\text{-bdb})_6]^{6+}$ metallacyclic rings are formed; the extended connection of the $[Ag_6(\mu\text{-bdb})_6]^{6+}$ units generate highly undulating cationic 2D sheets with a **6^3-hcb** network (Figure 2a,b). The 2D sheets extend in the *bc* plane and are packed along the *a* axis in an *AAA* manner. The triflate ions remain uncoordinated between the highly wavy sheets. Because of the wavy character of the layers, the thickness of each sheet is of about 20 Å. Although the triflate ions remained uncoordinated, they contribute to weak intermolecular C−H···O interactions between the oxygen atoms of the triflate ions and the H atoms of methylene groups or pyrazolyl rings (Figure 2b and Table S2). The 2-D honeycomb structure of **2** is composed of μ-bbd ligands with two different types of conformation; they are shown in different colors in Figure 2b. The green color ligand is centrosymmetric, with an (Ag)N…N(Ag) distance of 8.81 Å and parallel pyrazolyl rings; the red color ligands are shorter than the green in length, with an N…N distance of 8.20 Å, and exhibit a dihedral angle between the planes of the two pyrazolyl rings of 10.2°. The different conformations of the ligands cause two different Ag···Ag separations (10.04 and 7.28 Å).

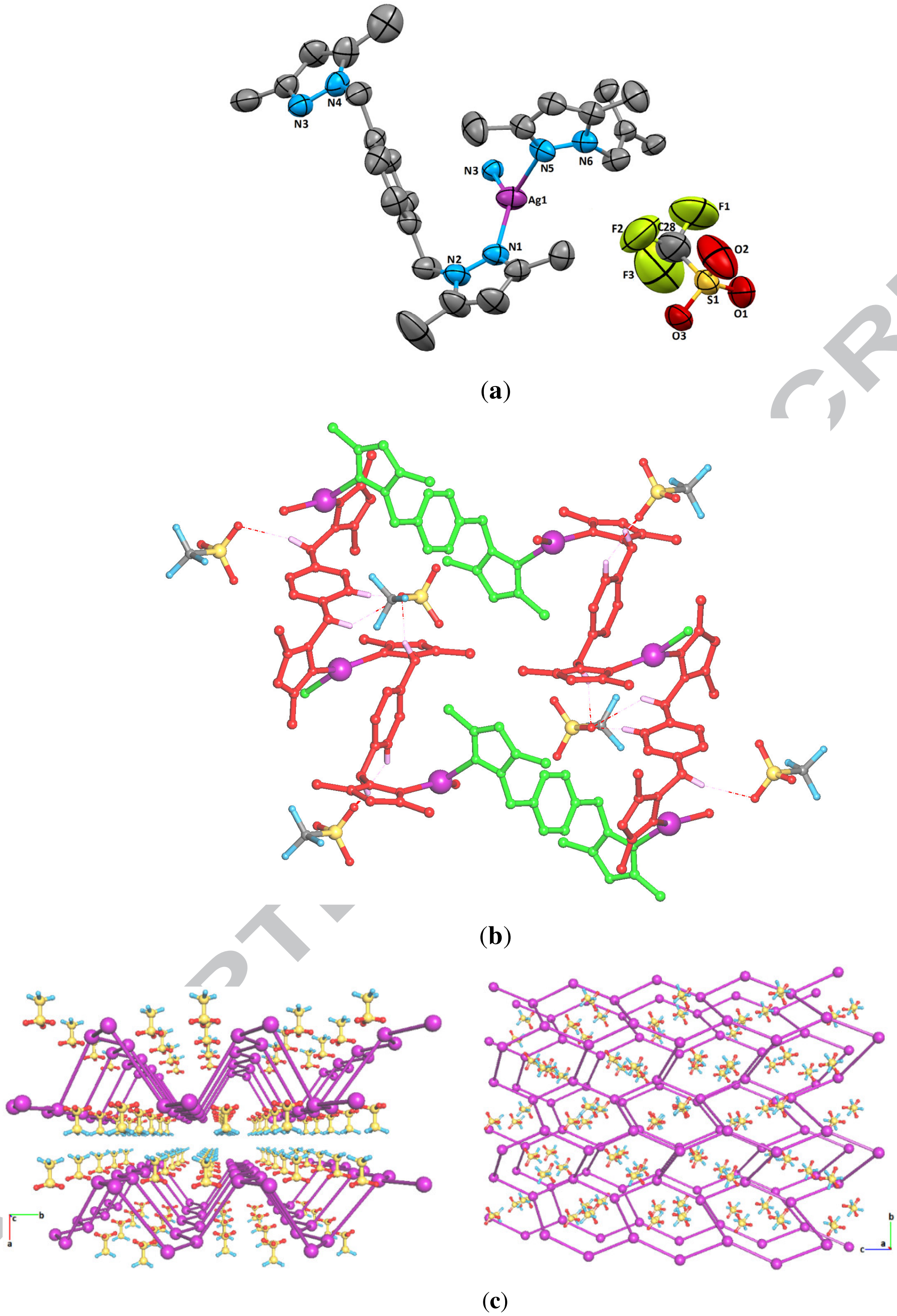
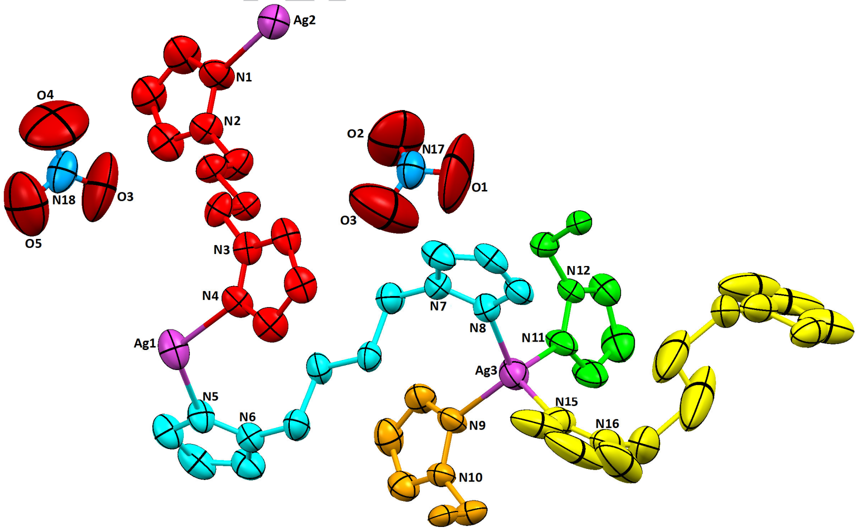


Figure 2. The structure of $\{[Ag(\mu\text{-bdb})_{1.5}](SO_3CF_3)\}_n$ (**2**). (a) Asymmetric unit with the numbering scheme for the non-H and -C atoms (b) Ball and stick representation of the cationic 66-membered $[Ag_6(\mu\text{-bdb})_6]^{6+}$ metallacyclic ring, showing two different conformations for the bdb linkers and non-classic C–H···O interactions between the triflate ions and the H atoms of the ligand (c) Schematic

representation of the wavy honeycomb sheets along the *c* (left) and *a* (right) axes together with the position of the $SO_3CF_3^-$ ions.

3.2.3. Crystal structure of $\{[Ag(\mu\text{-bpb})_2](NO_3)\}_n$ (3)

Compound **3** crystallizes in the monoclinic space group P2/c with Z= 8 (Table 1). The structure consists of cationic two-dimensional polymeric sheets and an uncoordinated nitrate counteranions, NO_3^- (Figure 3). The cationic 2-D sheets are composed of four coordinated silver(I) ions and μ-bpb as linker ligands. A closer inspection of the crystal structure shows that the unit cell is composed of five crystallographically independent bpb ligands, three silver(I) ions and two different nitrate counterions (Figure 3a, b). All the silver ions are coordinated by four pyrazolyl nitrogen atoms from μ-bpb ligands in a distorted tetrahedral ZnN_4 coordination geometry. Deviations from an ideal tetrahedral geometry can be specified by the τ_4 value [17]. The values of τ_4 for perfect tetrahedral and trigonal pyramidal geometries are 1.00 and 0.85, respectively. The calculated τ_4 values of 0.83, 0.82 and 0.82 for the Ag1, Ag2 and Ag3 ions, respectively, show a geometry closer to trigonal pyramidal (Figure 3c).



(**a**)

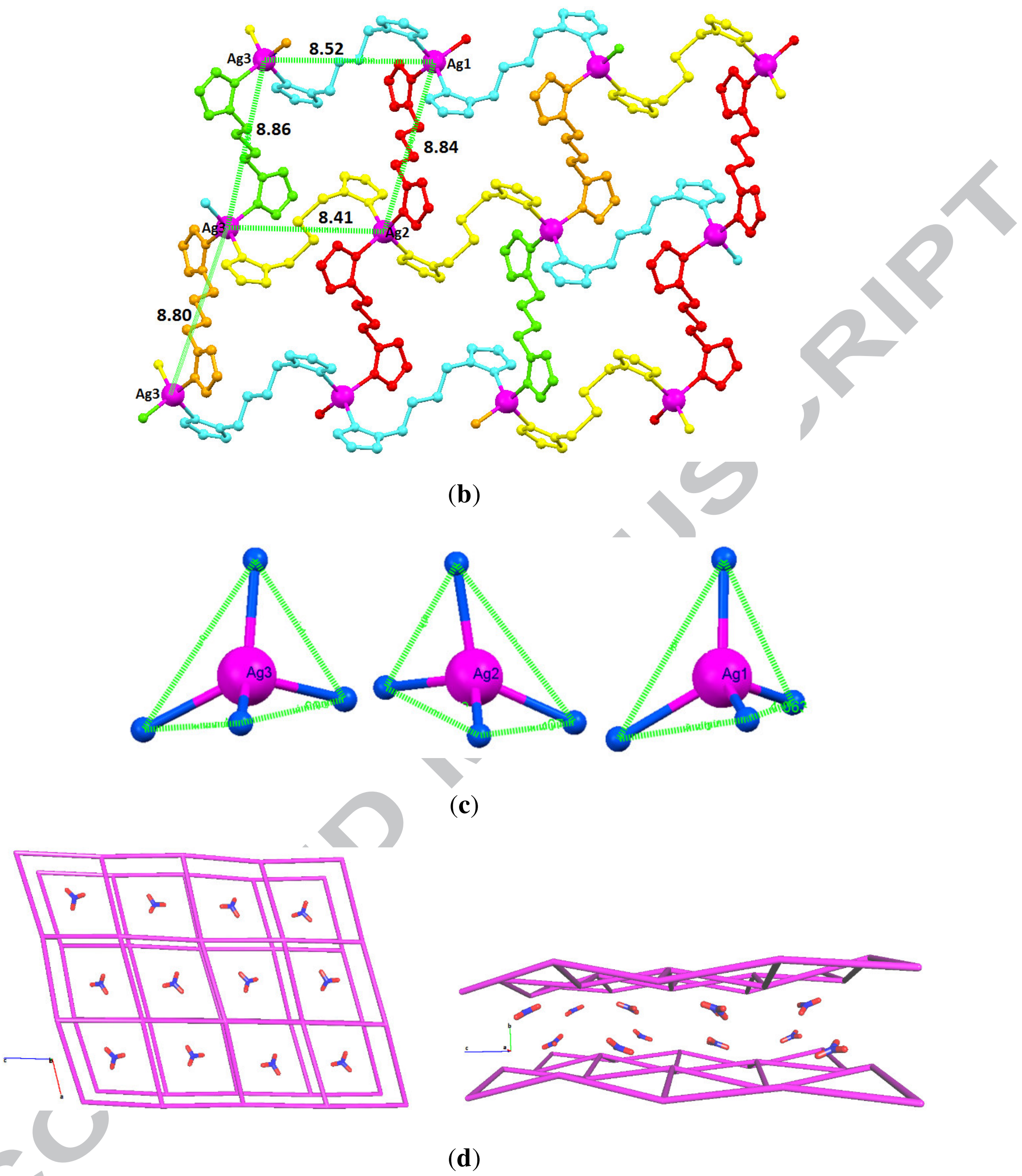


Figure 3. The structure of $\{[Ag(\mu\text{-bpb})_2](NO_3)\}_n$ (**3**). (a) Asymmetric unit with the numbering scheme for the non-H and -C atoms (b) Ball and stick representation of a 2D square layer, showing the five different conformations for the bpb linkers and the resulting five different Ag•••Ag distances (square window edges) (c) Coordination environments of the three independent silver(I) ions. (d) Schematic representation of the **4^4-sql** structure of **3** along the *b* (left) and *a* (right) axes together with the position of the nitrate ions.

The geometries of the five bpb linkers are summarized in Table 2. Four of the bpb ligands show the same *anti-anti-anti (aaa)* conformation, whilst one, the yellow colored one in Figure 3, which exhibits a *gauche-anti-gauche (gag)* conformation. For this reason, the length of the yellow bpb (6.96 Å) is almost 1 Å shorter than the lengths of the other bpb linkers (7.64-7.85 Å). From a topological point of view, each Ag(I) ion can be considered as a four-connected node. The connection of the silver(I) ions by the bpb linkers form a two-dimensional sheet structure with a 4^4-**sql** net. The different lengths of the linkers cause different Ag•••Ag distances (8.41-8.86 Å) in the 2D net structure of **3** (Figure 3b).

Table 2. Conformation, torsion (˚), dihedral angles (˚), N-to-N and Ag•••Ag separations (Å) for the bpb linker ligands in the structure of **3**.

Ligand	**Yellow**	**Green**	**Blue**	**Red**	**Orange**
Conformation	*gag*[b]	*aaa*	*aaa*	*aaa*	*aaa*
NCCC	51.18	177.42	179.48	179.14	178.69
CCCC	176.91	180	178.50	178.82	180
CCCN	-53.30	-177.42	-178.34	-176.83	-178.69
Dihedral angle[a]	2.31	0	2.40	4.80	0
N-to-N	6.96	7.848	7.639	7.792	7.739
Ag···Ag	8.41	8.862	8.522	8.841	8.798

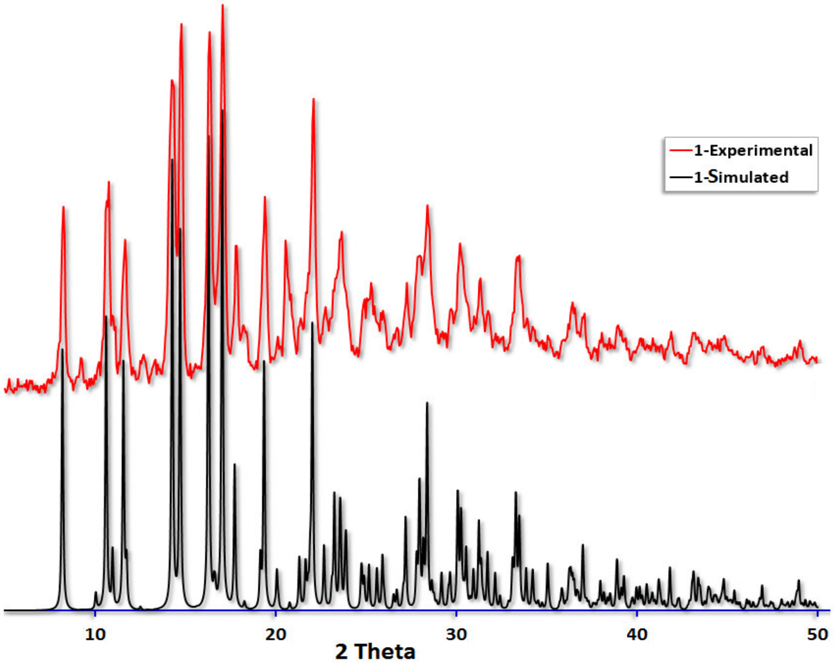
[a] Dihedral angle between the mean planes of pyrazolyl rings belonging to the same bpb ligand.
[b] *gauche* refers to torsion angles comprised between 30°/90° and -30°/-90°; *anti* to torsion angles comprised between +/- 90° and 180°.

The 2D square layers extend in the crystallographic *ac* plane and pack along the *b* axis with an *AAA* sequence, forming 1D channels across the 2D sheets (Figure 3d). The nitrate ions are located along the channels at the center of the square windows and between adjacent 2D sheets. There is no significant interaction between the NO_3^- anions and the Ag(I) centers. However, a closer inspection shows that there are weak C-H···O hydrogen bonds, with C-H···O distances of 2.32-2.40 Å, between two oxygen atoms of the nitrate anions and H atoms of the pyrazolyl rings or butyl spacers (Figure S2). Details of the hydrogen bonding geometries are given in Table S2. No remarkable short contacts or π···π interactions are found between adjacent sheets. Analysis of the structures by the Platon software [18] confirms no accessible void for guest molecules.

3.3. Spectroscopic characterization

The FT-IR spectra of coordination polymers **1-3** are shown in Figure S3. The stretching vibration of C=N bonds typical of the pyrazolyl rings of the linkers is present at 1517 (bpmb in **1**), 1550 (bdb in **2**) and 1512 (bpb in **3**) cm^{-1}. The location of the peaks depends on the type of substituents of the pyrazolyl rings. Therefore, the C=N stretching vibrations of the bdb linker, with two methyl substituents on the pyrazolyl rings, are present at higher wavenumbers compared to the bpb and bpmb ligands without Me substituents on the rings. The other peaks at 3120 (bpmb in **1**), 3128 (bdb in **2**) and 3107 and 3128 cm^{-1} (bpb in **3**) are assigned to the stretching vibration of aromatic C-H bonds of the coordinated ligands. Symmetric and asymmetric stretching vibrations of the methylene (–CH_2–) and methyl (-CH_3) groups of the linkers are observed in the region 2867-2950 cm^{-1}. In addition, the infrared spectra of the compounds show the characteristic bands of the counter anions. The sharp bands at 1262 (in **1**) and 1257 and 1275 (in **2**) cm^{-1} are attributed to the asymmetric $\nu_{as}(SO_3)$ stretching modes of the $CF_3SO_3^-$ anions [19]. The symmetric $\nu_s(SO_3)$ stretching bands of the triflate anions appear at 1030 cm^{-1} (for **1** and **2**), while the asymmetric $\nu_s(CF_3)$ and symmetric $\nu_{as}(CF_3)$ stretching bands appear at 1224 and 1160 (for **1**) and 1224 and 1153 (for **2**) cm^{-1}, respectively [19]. The results confirm the non-coordinating character of the triflate anions in the structures of **1** and **2**. The band at 1379 cm^{-1} in the infrared spectrum of **3** is assigned to the stretching vibrational mode of the uncoordinated NO_3^- anions.

In order to confirm the phase purity of the bulk materials, powder X-ray diffraction (PXRD) experiments were carried out for compounds **1**-**3**. The PXRD patterns are consistent with their simulated patterns (Figure 4). The results also show a higher crystallinity of the product **3**.



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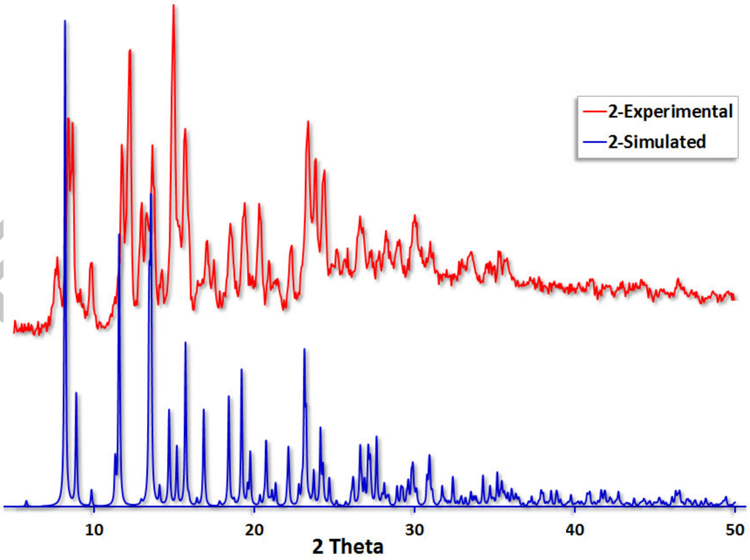

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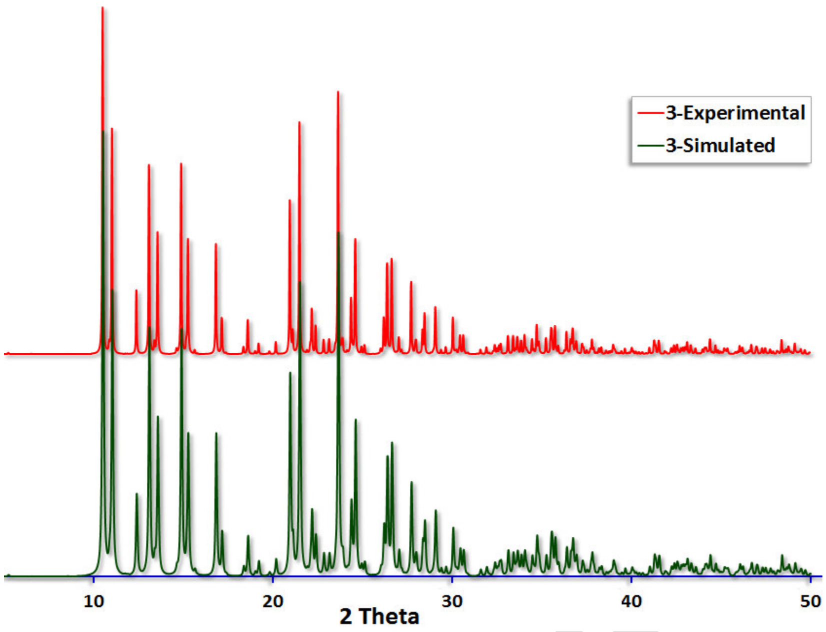

(c)

Figure 4. PXRD patterns for **1-3**. Calculated (from the single-crystal structure) and observed PXRD patterns for the bulk samples.

4. Conclusions

The self–assembly of silver(I) ions with flexible bidentate pyrazolyl-based linkers affords three new cationic silver(I) coordination polymers with different coordination environment of the metal ions, dimensionality and network topology of the structures. Interestingly, the results show that the steric hindrance of the donating groups of the ligands is not the only factor governing the geometries in these coordination compounds. However, an evaluation of the effects of anions and ligand conformation on the three structures is not straightforward, the three ligands being different. Nonetheless a comparison between compounds **1** and **2**, that have the same triflate anion and quite similar ligands, highlights the bulky effect of the methyl groups on the pyrazolyl ring of the bdb *vs*. bpmb ligands (see Scheme 1). this may be responsible for the different conformations of the ligands, resulting in a 2-coordination mode for silver atoms in **1** (shorter Ag-N...N-Ag distance for bpmb) compared to the 3-coordination mode in **2**. On the other hand, the more flexible bis(pyrazolyl) ligand and smaller nitrate anion in compound **3** may be responsible for the increase in the Ag coordination number to four, resulting in a **sql** topology compared to the **hcb** topology of compound **2** which shows a 3-coordination for the Ag atoms. Non-covalent weak interactions, such as hydrogen bonds and π···π stacking, also seem to be important structure-directing factors in the self-assembly of these silver(I) coordination polymers.

Appendix A. Supplementary data

CCDC 1532273-1532275 contain the supplementary crystallographic data for compounds **1**-**3**, respectively. 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

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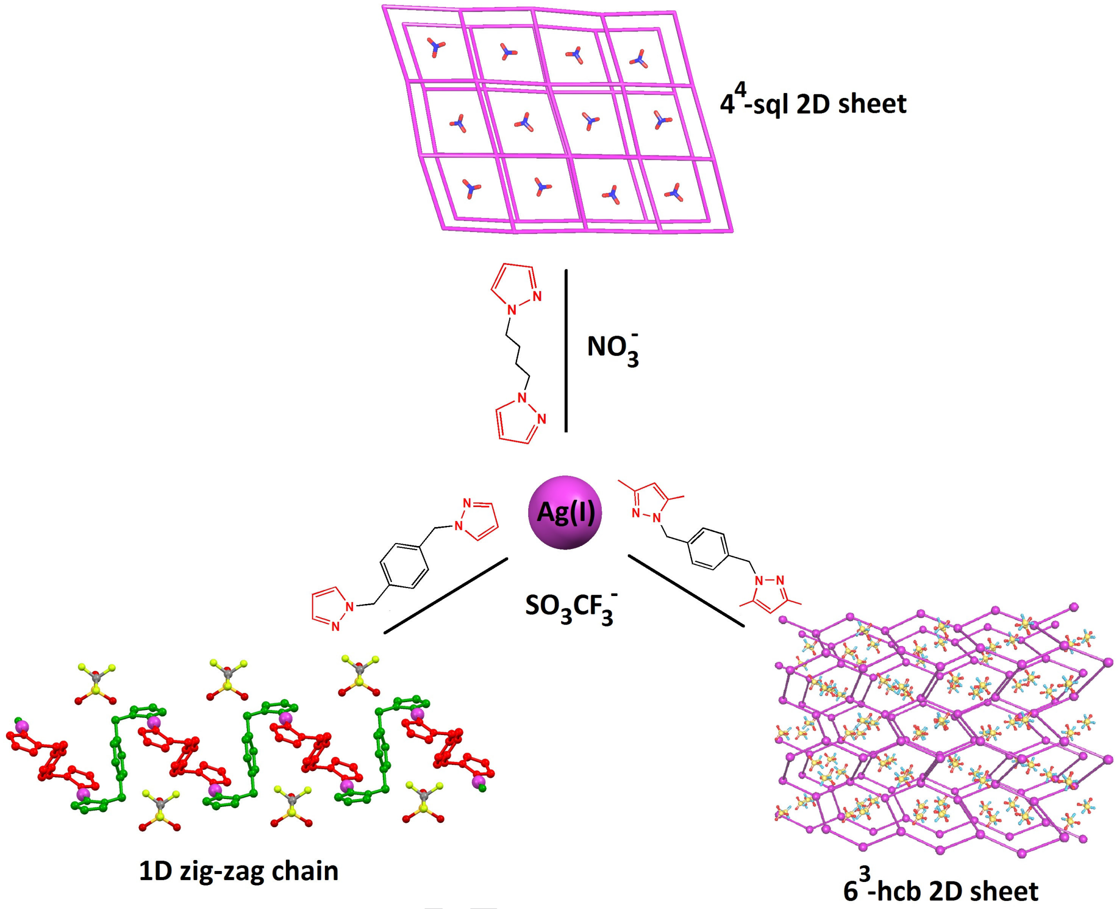
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$SO_3CF_3^-$
1D zig-zag chain
6^3-hcb 2D sheet

Three new cationic bis(pyrazolyl)-based silver(I) coordination polymers showing different metal coordination environments, dimensionalities and network topologies have been obtained and characterized.