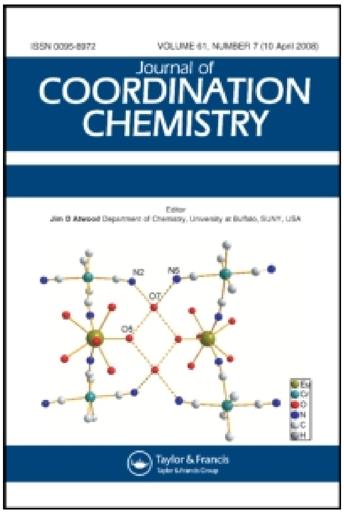

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Synthesis of 2-D graphite-like and 3-D diamond-like silver(I) polymers with 1,3-imidazolidine-2-thione

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Two metal–organic coordination polymers, $[Ag_2(imdt)_3(OAc)_2]_n$ (**1**) (imdt = 1,3-imidazolidine-2-thione, OAc = CH_3COO^-) and $[Ag(imdt)Cl]_n$ (**2**), were synthesized under similar conditions by using Et_3N (triethylamine) as buffering agent. X-ray diffraction shows that **1** crystallizes in the monoclinic system, $C2/c$ space group, $a = 13.822(5)$ Å, $b = 9.082(3)$ Å, $c = 16.965(6)$ Å, $V = 2114.2(14)$ Å^3, $Z = 8$, $D_c = 2.012\ g\ cm^{-3}$. Compound **2** crystallizes in the orthorhombic system, $P2_12_12_1$ space group, $a = 7.993(6)$ Å, $b = 7.993(6)$ Å, $c = 10.548(7)$ Å, $V = 673.9(7)$ Å^3, $Z = 4$, $D_c = 2.419\ g\ cm^{-3}$. Both **1** and **2** exhibit different architectures due to their different anions. Compound **1** shows a 2-D graphite-like network structure and **2** shows a 3-D diamond-like network structure.

Keywords: 1,3-Imidazolidine-2-thione; Silver polymers; Crystal structure

1. Introduction

Metal–organic coordination polymers have intriguing structural topologies and potential applications in heterogeneous catalysis, non-linear optics, magnetism, and gas storage [1, 2]. Compared to classical microporous inorganic materials such as zeolites, the structures of metal–organic coordination polymers can be controlled and the pores can be functionalized through modification of the walls. However, rational design and synthesis of metal–organic coordination polymers with unique structures and functions is difficult.

Silver(I) in particular has been used to construct geometrically and stereochemically interesting 1-D, 2-D, and 3-D infinite networks with coordination numbers ranging between two and six [3]. Careful selection of a suitable multifunction organic ligand containing a variety of bonding modes is very important; we introduce a flexible heterocyclic thioamide ligand, 1,3-imidazolidine-2-thione (imdt) for construction of metal–organic coordination polymers.

1,3-Imidazolidine-2-thione is well known in coordination chemistry. $[Au(imdt)_2]Cl \cdot H_2O$ was reported in 1928 [4]. Recently, imdt was found to induce DNA damage to liver, lungs, spleen, and kidneys in mice [5]. Our interests focus on

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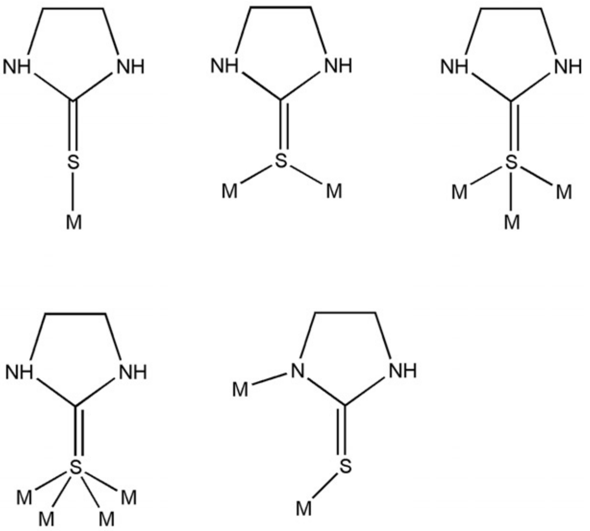

Scheme 1. Different coordination modes of imdt.

neutral imdt for two reasons. First, the exocyclic sulfur is capable of coordinating metals *via* η^1-S, μ_2-S, μ_3-S, and μ_4-S bonding modes, and as an anionic ligand it coordinates in a bridging μ-N, S mode (scheme 1) [6–9]. This versatility of imdt is attributed to the large size of the S. Second, the C=S can attach to a metal center at a variety of angles, forming helix or non-planar structures for different configurations.

In this article, we report syntheses and structures of two new silver polymers, $[Ag_2(imdt)_3(OAc)_2]_n$ (**1**) with 2-D graphite-like network structure and $[Ag(imdt)Cl]_n$ (**2**) with 3-D diamond-like network structure ($OAc^- = CH_3COO^-$), using this simple monothiolate to generate silver coordination polymers. Much work has focused on graphite-like and diamond-like 2-D and 3-D networks with functionalized channels or pores for selective absorption of gases or solvents [10]. However, it is rare to design 2-D graphite-like and 3-D diamond-like polymeric structures with the same ligand and metal [11].

2. Experimental

2.1. *Materials and instrumentation*

Reagents and solvents were commercially available and used as received. The C, H, and N microanalyses were carried out with a Vario EL elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 400–4000 cm^{-1} on a Bruker-EQUINOX 55 FT-IR spectrometer. Thermogravimetric (TG) data were collected on a Netzsch TG-209 analyzer in nitrogen at a heating rate of 10°C min^{-1}.

2.2. *Synthesis of $[Ag_2(imdt)_3(OAc)_2]_n$ (1)*

A mixture of AgOAc (0.042 g, 0.25 mmol) and imdt (0.0501 g, 0.5 mmol) was placed into a test tube containing DEF (*N*,*N*-diethylformamide, 5 mL). AgOAc was dissolved and the test tube was placed into a glass bottle containing ethanol (5 mL) and Et_3N (1 mL). The bottle was sealed and kept in a freezer (−2°C). Colorless crystals of **1** were obtained after allowing triethylamine vapor to diffuse into the DEF mixture for about a month (Yield: 62% on the basis of silver source). Crystals were collected by filtration and dried at room temperature. Anal. Calcd ($C_{13}H_{24}Ag_2N_6O_4S_3$): C, 26.91; N, 11.08; H, 3.99%. Found: C, 26.79; N, 10.92; H, 4.05%. FT-IR (KBr, cm^{-1}): ν(C–S) 1015s, ν(N–H) 3235m, ν(C–N) 1520s.

2.3. *Synthesis of [Ag(imdt)Cl]$_n$ (2)*

A mixture of AgCl (0.072 g, 0.5 mmol) and imdt (0.1022 g, 1 mmol) was placed into a test tube containing DEF (8 mL). AgCl was dissolved and the test tube was placed into a glass bottle containing Et_3N (10 mL). The bottle was sealed and kept in a freezer (−2°C). Colorless crystals of **2** were obtained after allowing triethylamine vapor to diffuse into the DEF mixture for about a month (Yield: 5% on the basis of silver source). Crystals were collected by filtration and dried at room temperature. Anal. Calcd ($C_3H_6AgClN_2S$): C, 14.68; N, 11.41; H, 2.46%. Found: C, 14.52; N, 11.55; H, 2.57%. FT-IR (KBr, cm^{-1}): ν(C–S) 1089s, ν(N–H) 3210m, ν(C–N) 1575s.

2.4. *X-ray crystallography*

Diffraction data for **1** and **2** were collected on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied using SADABS [12]. Structures were solved by direct methods and refined with a full-matrix least-squares technique using SHELXS-97 and SHELXL-97 [13]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The organic hydrogens were generated geometrically (C–H 0.96 Å and N–H 0.86 Å). Crystal data as well as details of data collection and refinement for the complexes are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structures*

3.1.1. [Ag_2(imdt)$_3$(OAc)$_2$]$_n$ (1). The 2-D polymeric structure of **1** was revealed by a single crystal X-ray diffraction study. Each silver is four-coordinate with three S atoms from three imdt ligands and one O from an OAc^- in a distorted tetrahedron (figure 1). (S(1)–Ag(1)–S(2) 112.63(3)°; O(1)–Ag(1)–S(1) 113.46(7)°; O(1)–Ag(1)–S(2) 86.19(7)°; O(1)–Ag(1)–S(2) 92.62(6)°; S(1)–Ag(1)–S(2) 105.50(4)°; S(2)–Ag(1)–S(2) 138.86(2)°). Compound **1** is a layered polymer with a graphite-like array of silver(I) ions. It has a 2-D lamella structure wherein the silvers are linked by sulfur of imdt and coordinated OAc^- to form inorganic layers and the imidazole rings of imdt produce the interlayer region (figure 2). The interlayer is 8.539 Å (based on the Ag $\cdots$ Ag distance). Each imdt in **1** is a μ_2 bridge linking two silvers through an S atom with Ag–S distances of 2.5858,

Table 1. Crystal and structure refinement data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{13}H_{24}Ag_2N_6O_4S_3$	$C_3H_6AgClN_2S$
Formula weight	640.30	245.48
Collection temperature T (K)	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$C2/c$	$P2_12_12_1$
Unit cell dimensions (Å, °)		
a	13.822(5)	7.993(6)
b	9.082(3)	7.993(6)
c	16.965(6)	10.548(7)
α	90.00	90.00
β	96.934(5)	90.00
γ	90.00	90.00
V (Å^3)	2114.2(14)	673.9(7)
Z	8	4
D_{Calcd} (g cm^{-3})	2.012	2.419
μ (mm^{-1})	2.181	3.589
Crystal size (mm^3)	0.35 × 0.28 × 0.20	0.28 × 0.20 × 0.15
Reflections collected	6366	2294
Independent reflection/R_{int}	2541/0.0260	1073/0.0298
Parameters	129	74
$R_1(I > 2\sigma(I))$[a]	0.0337	0.0278
R_1 (all data)[a]	0.0779	0.0559
$wR_2(I > 2\sigma(I))$[b]	0.0448	0.0305
wR_2 (all data)[b]	0.0830	0.0567
Goodness-of-fit on F^2	1.075	0.999
Residual density (e Å^{-3})	1.277/−1.005	0.674/−0.411

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $wR_2 = \sum\{[w(F_o^2 - F_c^2)]\sum[wF_o^2]^2\}^{1/2}$.

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

Compound **1**			
Ag(1)–O(1)	2.501(3)	S(1)–Ag(1)–S(2)	105.50(4)
Ag(1)–S(1)	2.5858(10)	S(2)#1–Ag(1)–S(2)	138.86(2)
Ag(1)–S(2)#1	2.6033(11)	C(1)–S(1)–Ag(1)	96.31(3)
Ag(1)–S(2)	2.6600(12)	C(1)–S(1)–Ag(1)#2	96.31(3)
S(1)–Ag(1)#2	2.5858(10)	Ag(1)–S(1)–Ag(1)#2	167.37(6)
S(2)–Ag(1)#3	2.6033(11)	C(5)–S(2)–Ag(1)#3	106.77(11)
O(1)–Ag(1)–S(1)	113.46(7)	C(5)–S(2)–Ag(1)	111.57(11)
O(1)–Ag(1)–S(2)#1	86.19(7)	Ag(1)#3–S(2)–Ag(1)	137.09(4)
S(1)–Ag(1)–S(2)#1	112.63(3)	C(6)–O(1)–Ag(1)	119.8(2)
O(1)–Ag(1)–S(2)	92.62(6)		
Compound **2**			
Ag(1)–S(1)	2.4866(14)	Cl(1)–Ag(1)–S(1)#1	110.91(5)
Ag(1)–Cl(1)	2.5035(18)	S(1)–Ag(1)–Cl(1)#2	102.75(5)
Ag(1)–S(1)#1	2.5219(14)	Cl(1)–Ag(1)–Cl(1)#2	111.93(5)
Ag(1)–Cl(1)#2	2.6800(18)	S(1)#1–Ag(1)–Cl(1)#2	95.56(6)
Cl(1)–Ag(1)#3	2.6800(18)	Ag(1)–Cl(1)–Ag(1)#3	144.74(7)
S(1)–Ag(1)#4	2.5219(14)	C(3)–S(1)–Ag(1)	108.51(16)
S(1)–Ag(1)–Cl(1)	113.81(6)	C(3)–S(1)–Ag(1)#4	104.51(16)
S(1)–Ag(1)–S(1)#1	119.83(4)	Ag(1)–S(1)–Ag(1)#4	140.46(6)

Symmetry transformations used to generate equivalent atoms.

Symmetry codes for **1**: #1: $-x+1/2$, $y-1/2$, $-z+1/2$; #2: $-x$, y, $-z+1/2$; #3: $-x+1/2$, $y+1/2$, $-z+1/2$.

Symmetry codes for **2**: #1: $-x$, $y-1/2$, $-z+3/2$; #2: $x-1/2$, $-y+3/2$, $-z+1$; #3: $x+1/2$, $-y+3/2$, $-z+1$; #4: $-x$, $y+1/2$, $-z+3/2$.

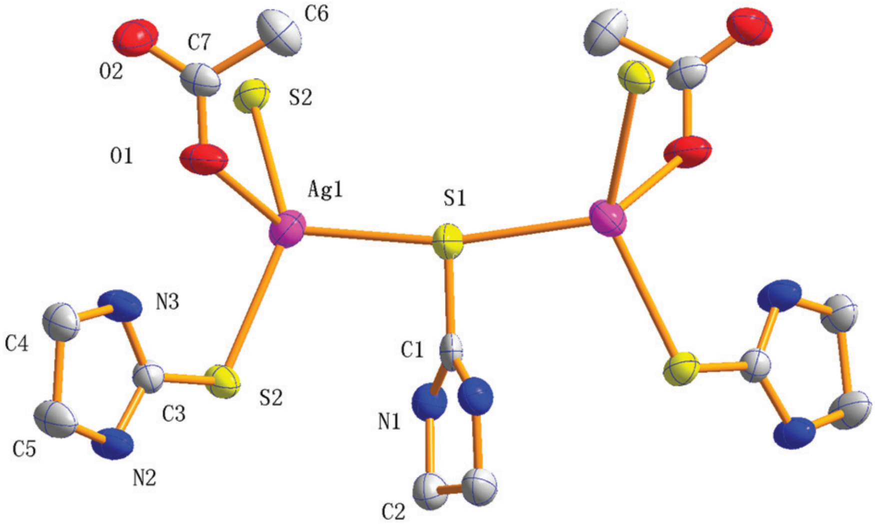

Figure 1. Molecular structure of **1** with thermal ellipsoids at 50% probability.

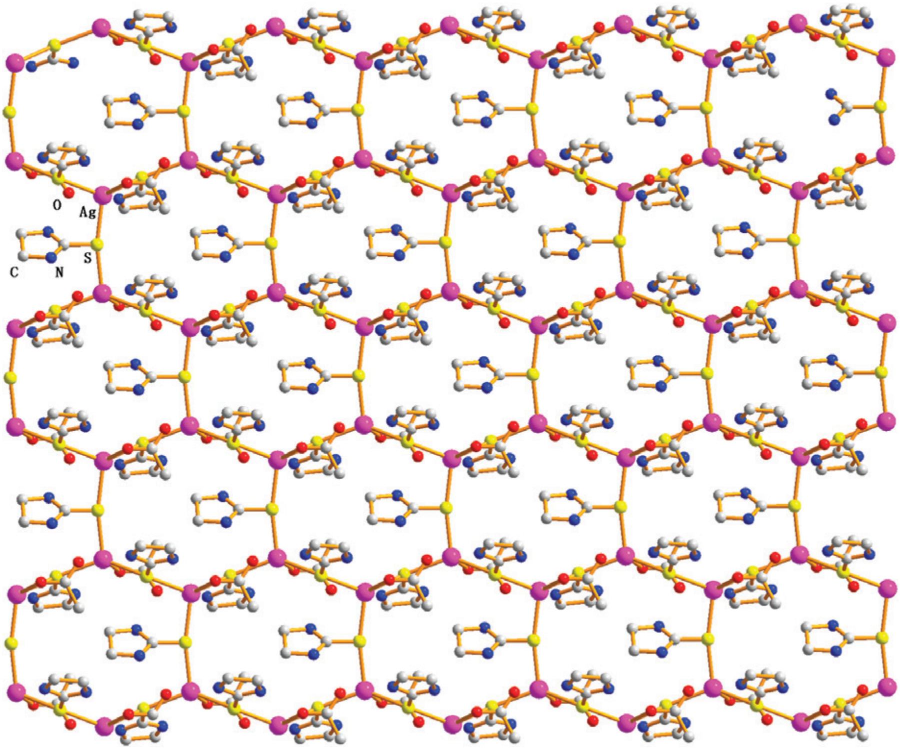

Figure 2. The lamella structure and graphite-like array of silver(I) ions in **1** along the *c*-axis (pink, Ag; red, O; blue, N; yellow, S; gray, C).

Table 3. The C=S bond lengths (Å) for **1** and **2**, and other related thioamide compounds.

Compound	C = S bond lengths (Å)	Ref.
Free ligand of imdt	1.693(6)	[6a]
$[Ag_2(imdt)_3(OAc)_2]_n$	S(1)–C(1) 1.728(5) S(2)–C(5) 1.716(3)	This work
$[Ag(imdt)Cl]_n$	S(1)–C(3) 1.707(5)	This work
$[ZnO(Meimdt)_6]$	1.726(13)	[7d]
$[Cu_6(imdt)_6X_6]_n$ (X = Br, I)	1.699–1.733	[8e]
$[Cu_2(imdt)_2(SCN)_2]_n$	1.722(5)	[9e]
$[Cu_6(\mu_3\text{-imdt})_4(\mu\text{-imdt})_2(\mu\text{-I})_2I_4]_n$	1.705(4)–1.724(4)	[9e]
$[Cu_2(\mu\text{- imdt})_2(\eta^1\text{-imdt})_2Br_2]$	1.699(2)–1.707(2)	[9e]

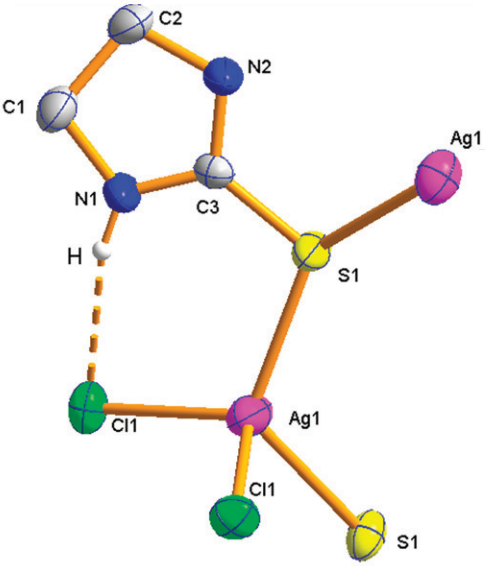

Figure 3. Molecular structure of **2** with thermal ellipsoids at 50% probability and the intramolecular hydrogen bond in **2**.

2.6033, and 2.6600 Å. The silvers of each layer are nearly coplanar in a graphite-like hexagonal motif (figure 2). The Ag_6 hexagon is somewhat distorted because of different Ag–Ag–Ag angles (110.90° and 135.95°). The Ag–Ag distances are 4.898 and 5.140 Å. The C–S bond distances, 1.716–1.728 Å, longer than the double-bond distance (C=S, 1.69 Å) of the free ligand and shorter than the single-bond distance (C–S, 1.81 Å), reveal considerable double-bond character (table 3).

3.1.2. $[Ag(imdt)Cl]_n$ (2). The 3-D polymeric structure of **2** contains four-coordinate silver centers linked to two sulfurs from two imdt and two Cl^-s (figure 3). Each silver(I) is a distorted tetrahedron of S_2Cl_2. Two AgS_2Cl_2 tetrahedra share one vertex (S or Cl), thus, either chloride or sulfur in the complex is μ_2-bridge linking two metal centers to form the diamond-like network structure. The average Ag–Ag separations are 4.8265 Å, precluding of direct metal–metal interaction. The average Ag–Cl bond distance (2.591(8) Å) is longer than that of Ag–S (2.504(3) Å). The average Cl–Ag–Cl angle

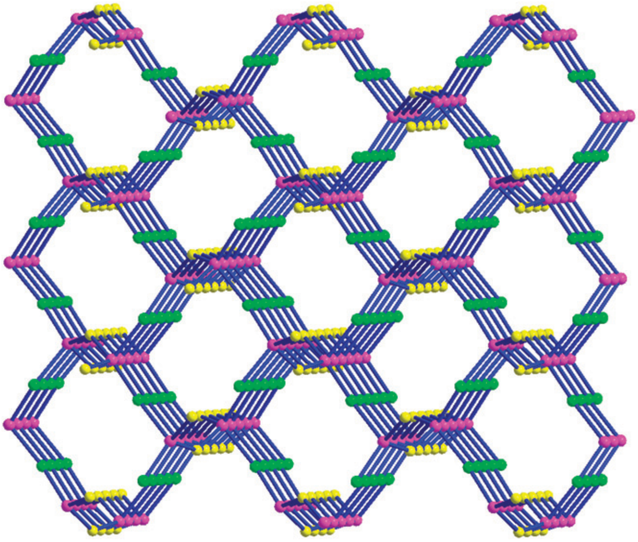

Figure 4. The 3-D diamond-like net in **2** along the *b*-axis (pink, Ag; yellow, S; green, Cl; all the hydrogen, nitrogen, and carbon atoms were omitted for clarity).

(111.9(4)°) is larger than that of Cl–Ag–S (105.7(6)°) but smaller than that of S–Ag–S (119.8(3)°). The Ag–Cl–Ag angle (144.7(5)°) is nearly the same as that of Ag–S–Ag (140.4(7)°). An efficient intramolecular N–H···Cl hydrogen bond occurs in each [Ag($SC_3H_6N_2$)Cl] building block in this crystal (figure 3), and the average N···Cl distance is 3.297 Å. The C–S bond distances, 1.707 Å, reveal considerable double-bond character (table 3).

A remarkable feature of **2** is the diamond-like array of silver(I) ions. From a topological perspective each Ag center serves as a four-connecting node within a 3-D network. The topology of the network is the same as that of diamond, although there is little resemblance with the idealized diamond net (figure 4).

3.2. *IR spectroscopy*

The ν(C–S) at 1210 cm^{-1} of the free ligand shifted to 1015 cm^{-1} in **1** and 1089 cm^{-1} in **2**. The ν(C–N) of free ligand at 1510 cm^{-1} shifted to 1540 cm^{-1} in **1** and 1575 cm^{-1} in **2**. Another important IR band of free ligand is ν(N–H) at 3240 cm^{-1}. Upon coordination to silver(I) this band shifts to 3235 cm^{-1} in **1** and 3210 cm^{-1} in **2**. The presence of a band around 3200 cm^{-1} in the free ligand, as well as the compounds, indicates the thione form of ligand in the solid state.

3.3. *Thermogravimetry*

Thermal analyses on **1** (Supplementary material) exhibit two steps of weight loss. The first starting at *ca* 130–175°C gives a total loss of *ca* 15.22%, corresponding to loss of one imdt per formula unit. The second weight loss at *ca* 176–244°C gives a total loss of *ca* 33.03%, corresponding to loss of another two imdt molecules. The final pyrolysis was completed at 330°C, giving a Ag_2CO_3 powder. There is only one weight loss for **2** (Supplementary material) of 40.11% between 249 and 337°C, corresponding to imdt ligands (Calcd: 41.55%).

4. Conclusion

Two coordination polymers with distinct architectures were synthesized from 1,3-imidazolidine-2-thione and Ag(I) ions. Compound **1** shows a 2-D graphite-like network and **2** shows a 3-D diamond-like structure. The coordination anions play an important role in the structural difference since the both the compounds use Ag. The acetate in **1** occupies one Ag coordination site, but does not connect other Ag's. In **2**, every chloride connects two Ag atoms, forming a 3-D structure. Our interests are pointing at testing different coordination anions in order to get new Ag and imdt coordination compounds. It is easy to change Ag salts and further experiments are in progress [14].

Supplementary material

CCDC 609373 and 609374 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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