

## SUPPORTING INFORMATION

### **1,2,4,5-Tetrazine: An unprecedented $\mu_4$ -coordination that enhances ability for anion/ $\pi$ interactions**

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#### **Unsubstituted 1,2,4,5-tetrazine.**

Recently we have reported very easy procedure for the preparation of this substance, which is optimized for 2 working days and as adaptation for the university practicum (electronic supplementary material for publication: K.V. Domasevitch, I.A. Gural'skiy, P.V. Solntsev, E.B. Rusanov, H. Krautscheid, J.A.K. Howard and A.N. Chernega. *Dalton Trans.*, 2007, 3140).

This substance may be stored in a refrigerator without decomposition and easily handled.

It is extremely volatile even at r.t. and it can be purified by vacuum sublimation at r.t. on a cooling finger (see the above reference).

*Heating of 1,2,4,5-tetrazine may effect explosion!* (Review: D.E. Chavez, M.A. Hiskey and D.L. Naud, *Propellants, Explosives, Pyrotechnics*, 2004, **29**, 209)

## Crystallography

The intensity data were collected at 213 K on a Stoe Imaging Plate Diffraction System [1]:  $\phi$  oscillation scans 0–180°, step  $\Delta\phi = 1.0^\circ$  ( $\phi = 0$ –220° for **4**, and  $\Delta\phi = 0.8^\circ$  for **5**) (graphite monochromated Mo-K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ; numerical absorption corrections using X-RED [2] and X-SHAPE [3]). The structures were solved by direct methods and refined in the anisotropic approximation using SHELXS-97 [4] and SHELXL-97 [5]. Details are given below. Graphical representation of the crystal structures was made using program Diamond [6].

1. Stoe & Cie (2000). *IPDS Software*. Stoe & Cie GmbH, Darmstadt, Germany.
2. Stoe & Cie (1999). X-RED. Version 1.22. Stoe & Cie GmbH, Darmstadt, Germany.
3. Stoe & Cie (2001). X-SPAPE. Revision 1.06. Stoe & Cie GmbH, Darmstadt, Germany.
4. G.M. Sheldrick, *Acta Crystallogr.*, 1990, **A46**, 467.
5. G.M. Sheldrick, SHELXL97, A system of computer programs for X-ray structure determination, University of Göttingen, Göttingen, Germany, 1997.
6. K. Brandenburg, Diamond 2.1c, Crystal Impact GbR, Bonn, 1999.

### Refinement of the structures

**Structure [Ag(ttz)(NO<sub>3</sub>)] (1).** The coordinated nitrate anion is disordered over two mirror-plane related positions (See Figs. S1 and S2). The disorder was refined without any restraints in geometry and in anisotropic approximation. The only unique hydrogen atom was located and refined isotropically leading to a reasonable CH bond of 0.94 Å and  $U_{\text{iso}} = 0.036 \text{ \AA}^2$ .

**Structure [Ag(ttz)(ClO<sub>4</sub>)] (2).** The hydrogen atom was located from difference maps and then refined as riding, with C---H distance constrained to 0.94 Å, and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  (parent carbon atom).

Chlorine atom of the perchlorate anion is situated on intersection of two mirror planes (site letter 4e). Oxygen atoms of the anion reside in general positions and are equally disordered over two crystallographically independent orientations. In total this affords disordering of the oxygen atoms over 8 positions. The disorder was readily resolved and refined with a set of soft restraints for geometry of ClO<sub>4</sub>, the ordered Cl atom was refined anisotropically and the oxygen atoms were left isotropic. Subsequent refinement led to a perfect convergence and very reasonable isotropic U values for all oxygen atoms ( $U_{\text{iso}} = 0.051$ – $0.101 \text{ \AA}^2$ ). Scheme of the disorder is described in Figs. S3–S5.

**Structure [Ag<sub>2</sub>(Me<sub>2</sub>ttz)(NO<sub>3</sub>)<sub>2</sub>] (3).** The hydrogen atoms of the methyl groups are disordered over a mirror plane and therefore these atoms were modeled considering idealized

geometry of the disordered methyl group [C---H constrained to 0.97 Å, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$  (parent carbon atoms)].

**Structure [Ag<sub>2</sub>(Me<sub>2</sub>ttz)(H<sub>2</sub>O)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>] (4).** The refinement was standard. All H atoms were located from difference maps and then fixed with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$  (parent methyl carbon atom or water oxygen atom) leading to the standard separations C---H (methyl) 0.956-0.962 Å and OH 0.851 Å. Figure S8 and Table S1 provide information on a hydrogen bonding in the structure.

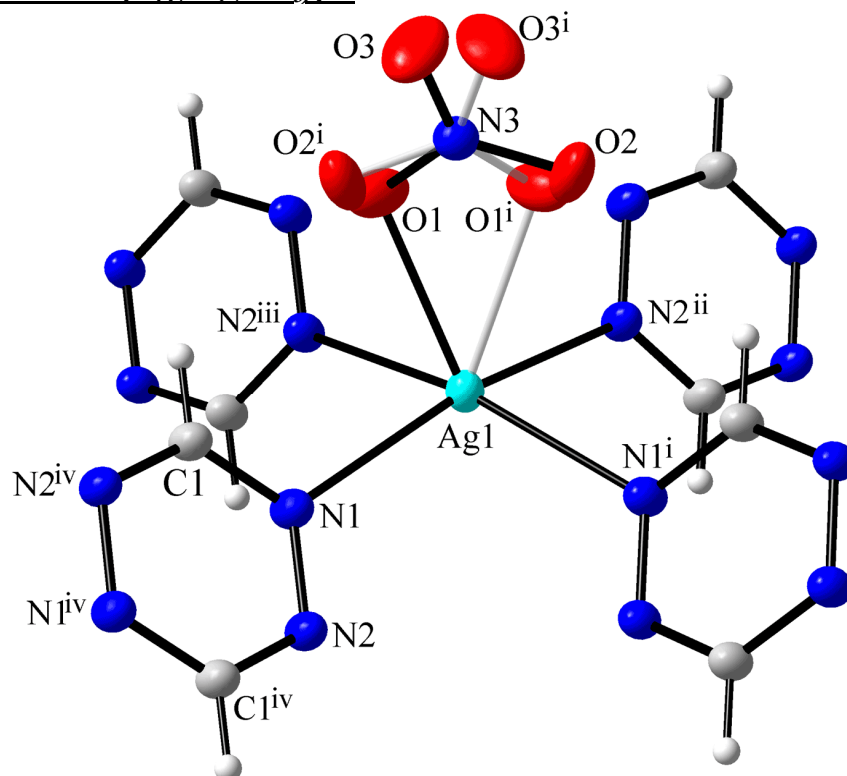
**Structure [Ag<sub>6</sub>(Me<sub>2</sub>ttz)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>6</sub>] (5).** Structure comprises three independent tetrazine molecules (two of which are crystallographically centrosymmetric), six silver and triflate ions (See Figs. S9-S11).

The refinement was essentially standard. However, high residual electron density near three of six silver ions suggested possible twinning or disordering of the silver ions over two closely separated positions (0.40-0.71 Å). It was not possible to refine such models satisfactory.

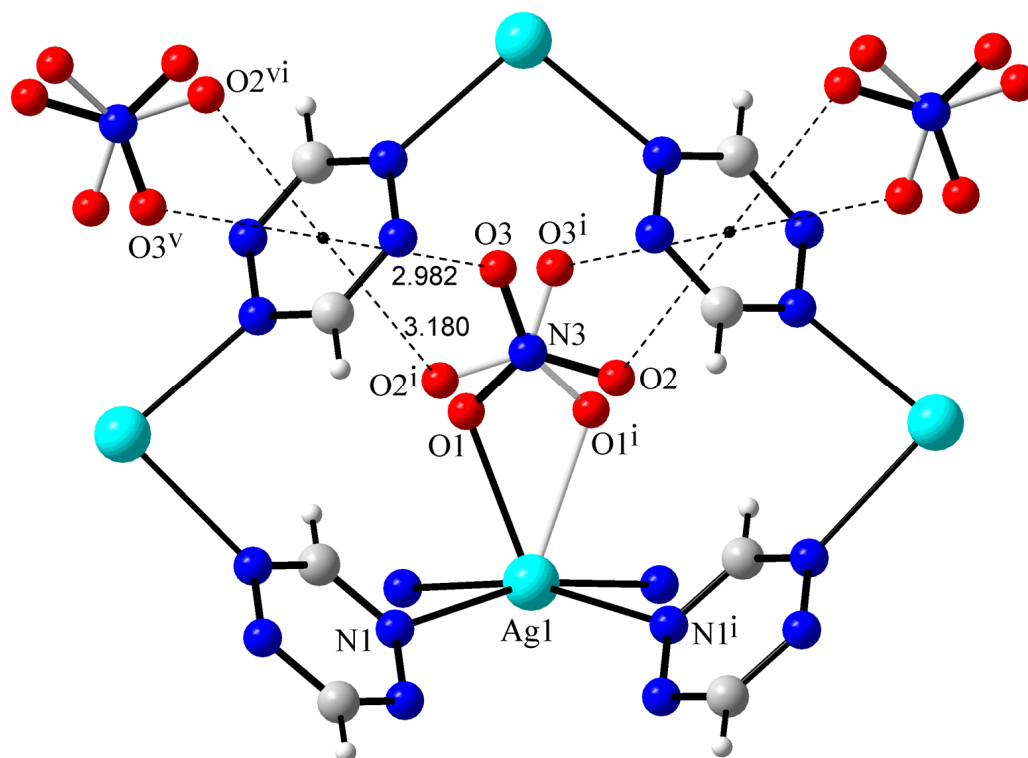
Relatively high anisotropy for thermal motion of O and F atoms of two triflate anions possibly indicates their disordering, however we were not successful to resolve it. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms of methyl groups and water molecules were added geometrically with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$  (parent methyl carbon atom or water oxygen atom).

**Structure [Cu<sub>4</sub>Cl<sub>4</sub>(Me<sub>2</sub>ttz)] (6).** The refinement was standard. CH<sub>3</sub> hydrogen atoms were added geometrically with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}$  (parent carbon atom).

**Structure [Ag(ttz)(NO<sub>3</sub>)] 1**



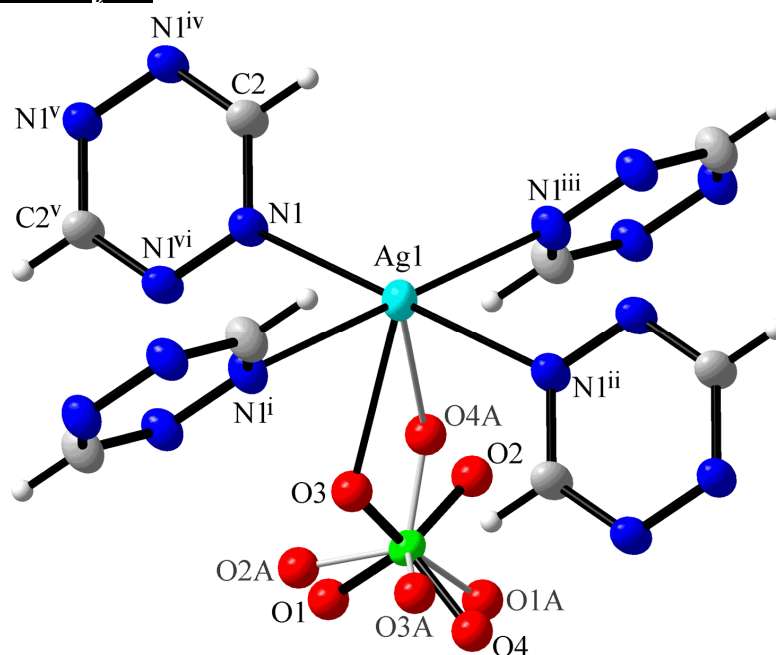
**Figure S1.** Distorted tetragonal-pyramidal coordination environment of the silver ion in the structure of **1**. Thermal ellipsoids are drawn at the 40% probability level. The coordinated nitrate anion is equally disordered over a mirror plane. Symmetry codes: (i)  $x, 1.5-y, z$ ; (ii)  $0.5+x, 1.5-y, 0.5-z$ ; (iii)  $0.5+x, y, 0.5-z$ ; (iv)  $1-x, 1-y, -z$ .



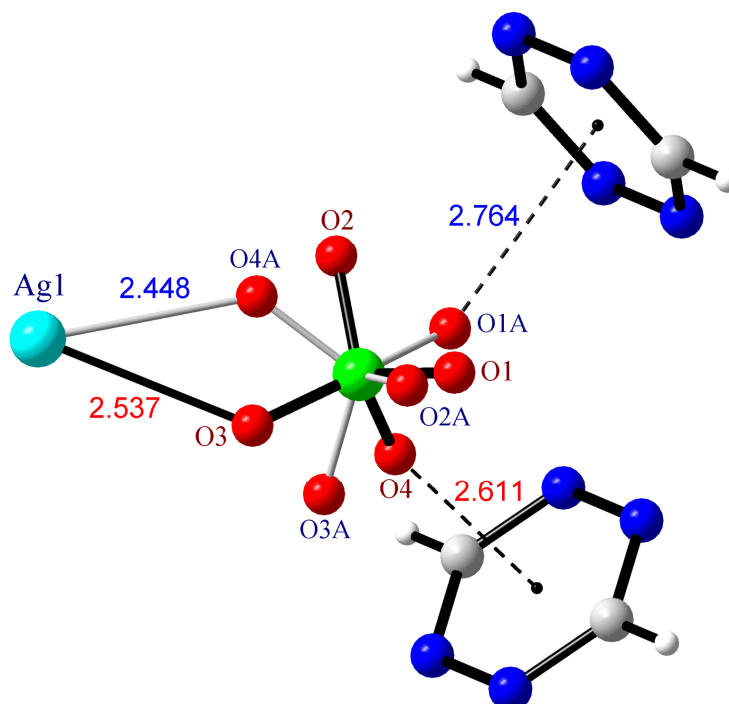
**Figure S2.** Fragment of the structure of **1**, showing the nitrate anion in the electrophilic environment. Symmetry codes: (i)  $x, 1.5-y, z$ ; (v)  $2-x, 1-y, -1-z$ ; (vi)  $2-x, -0.5+y, -1-z$ .

Note that two orientations of the disordered anion are symmetry equivalent and in each case the nitrate maintain two short  $O\cdots\pi$  contacts with electron deficient tetrazine. The tetrazine molecule forms such contacts at two axial sides simultaneously.

**Structure [Ag(ttz)(ClO<sub>4</sub>)] 2**

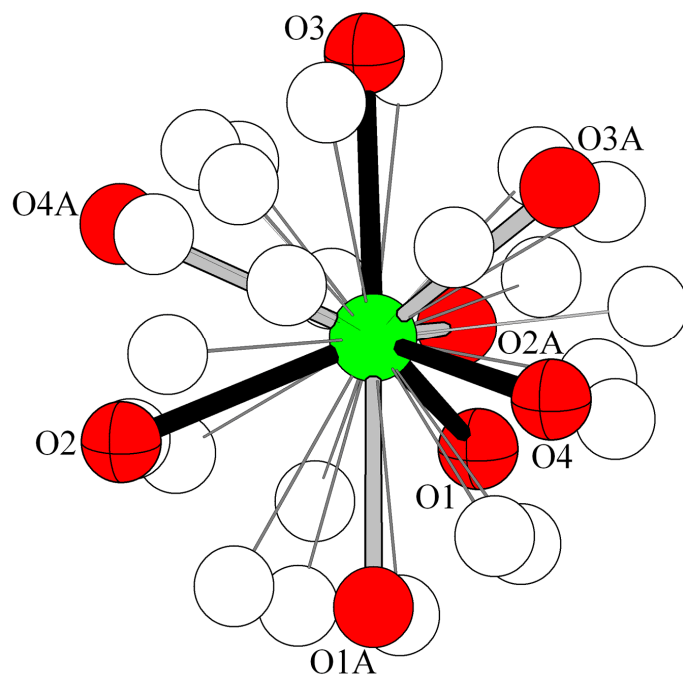


**Figure S3.** Coordination environment of the silver ion in structure of **2**, showing two orientations for the perchlorate disorder. Thermal ellipsoids are drawn at the 40% probability level, the oxygen atoms were refined isotropically. Symmetry codes: (i)  $x, 1.5-y, z$ ; (ii)  $0.5-x, 1.5-y, 0.5-z$ ; (iii)  $0.5-x, y, 0.5-z$ ; (iv)  $x, 1-y, -z$ ; (v)  $-x, 1-y, -z$ ; (vi)  $-x, y, z$ .



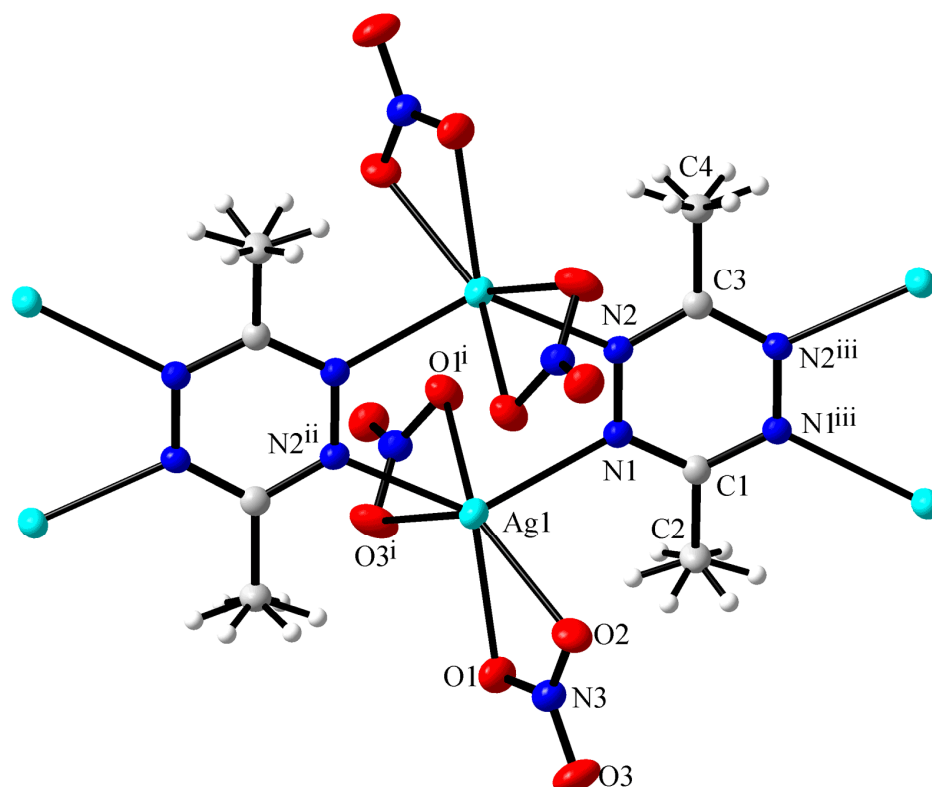
**Figure S4.** Fragment of the structure of **2**, showing how the perchlorate anion is involved into coordination and anion/ $\pi$  interaction. For two orientations of the anion, a shorter Ag-O distance corresponds to a slightly more distal (but still exceptionally short!) anion/ $\pi$  stacking. In this sense, two types of interactions (Ag-O and  $O\cdots\pi$ ) are competitive and equally responsible for situation of the perchlorate in the lattice.

Note that the site of chlorine atom corresponds to intersection of two crystallographic mirror planes and this effects disordering for each of the orientations of perchlorate anion over four positions. These positions are symmetry-related and therefore for each of them the oxygen atoms generate the same set of Ag-O and O--- $\pi$  interactions, as is depicted in the figure.

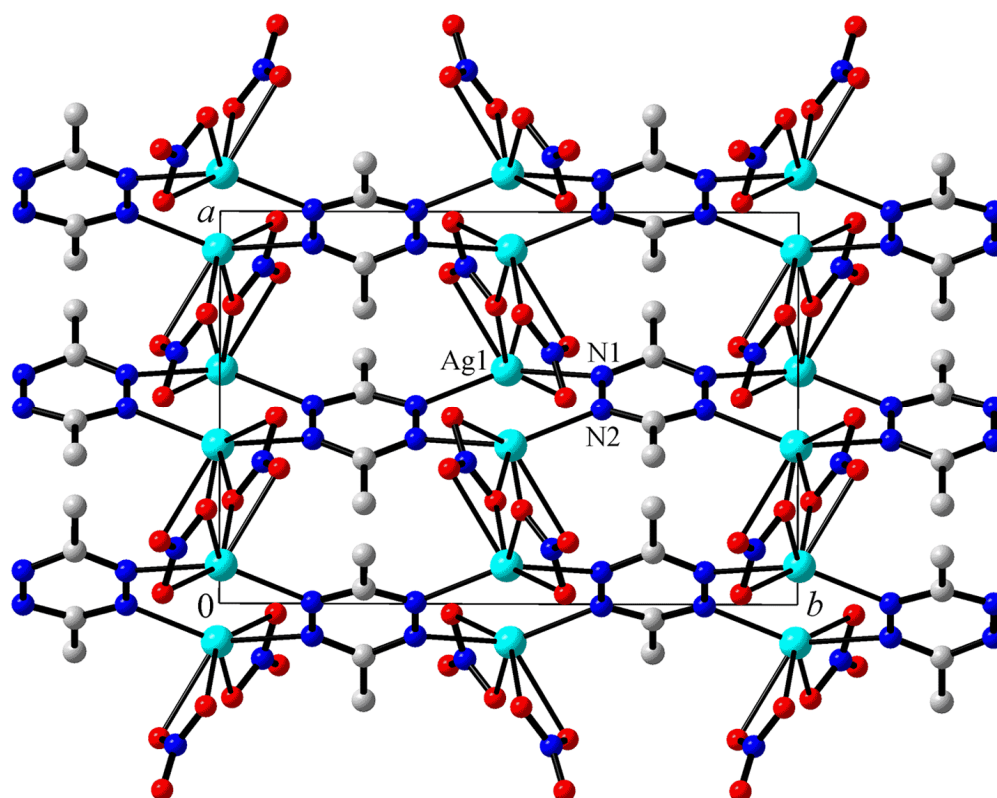


**Figure S5.** The disordering scheme for the perchlorate anion. Oxygen atoms of two crystallographically independent orientations are shaded red.

**Structure [Ag<sub>2</sub>(Me<sub>2</sub>ttz)(NO<sub>3</sub>)<sub>2</sub>] 3**

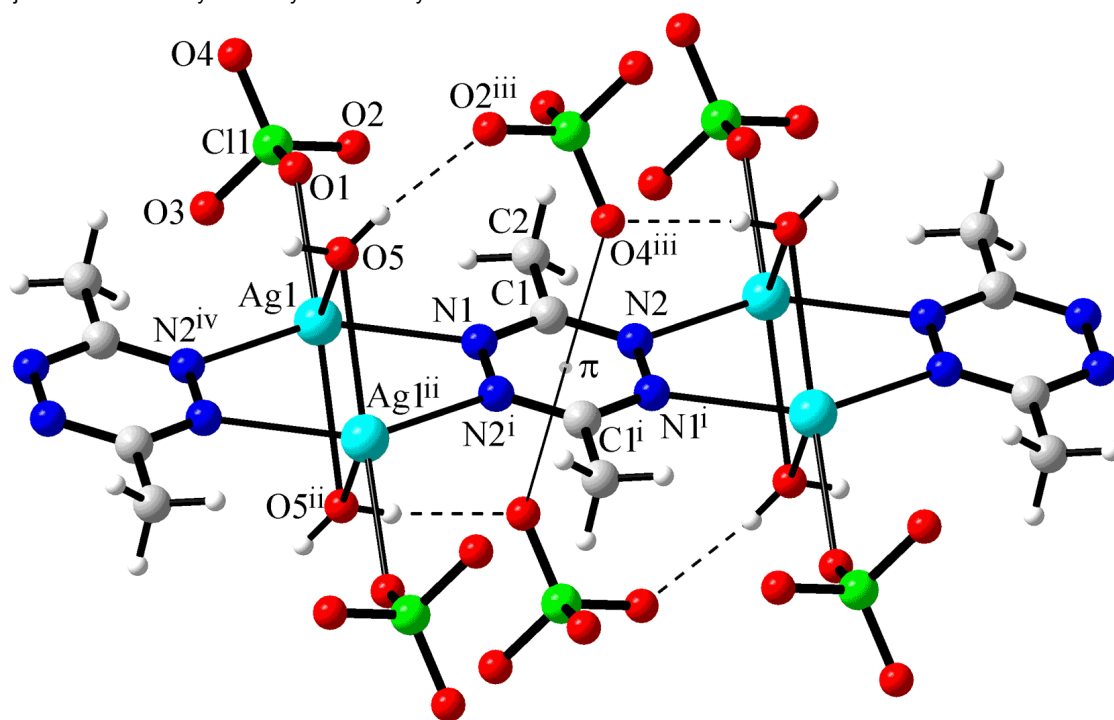


**Figure S6.** Fragment of the structure of **3**, showing coordination environment of the silver atoms. Thermal ellipsoids are drawn at the 40% probability level. Symmetry codes: (i)  $1.5-x, 1-y, -0.5+z$ ; (ii)  $1-x, 1-y, -z$ ; (iii)  $x, 1.5-y, z$ .



**Figure S7.** Projection of 3D structure of **3** on *ab* plane, showing bridging function of tetradentate nitrate anions.

*Structure*  $[Ag_2(Me_2ttz)(H_2O)_2(ClO_4)_2] \cdot 4$

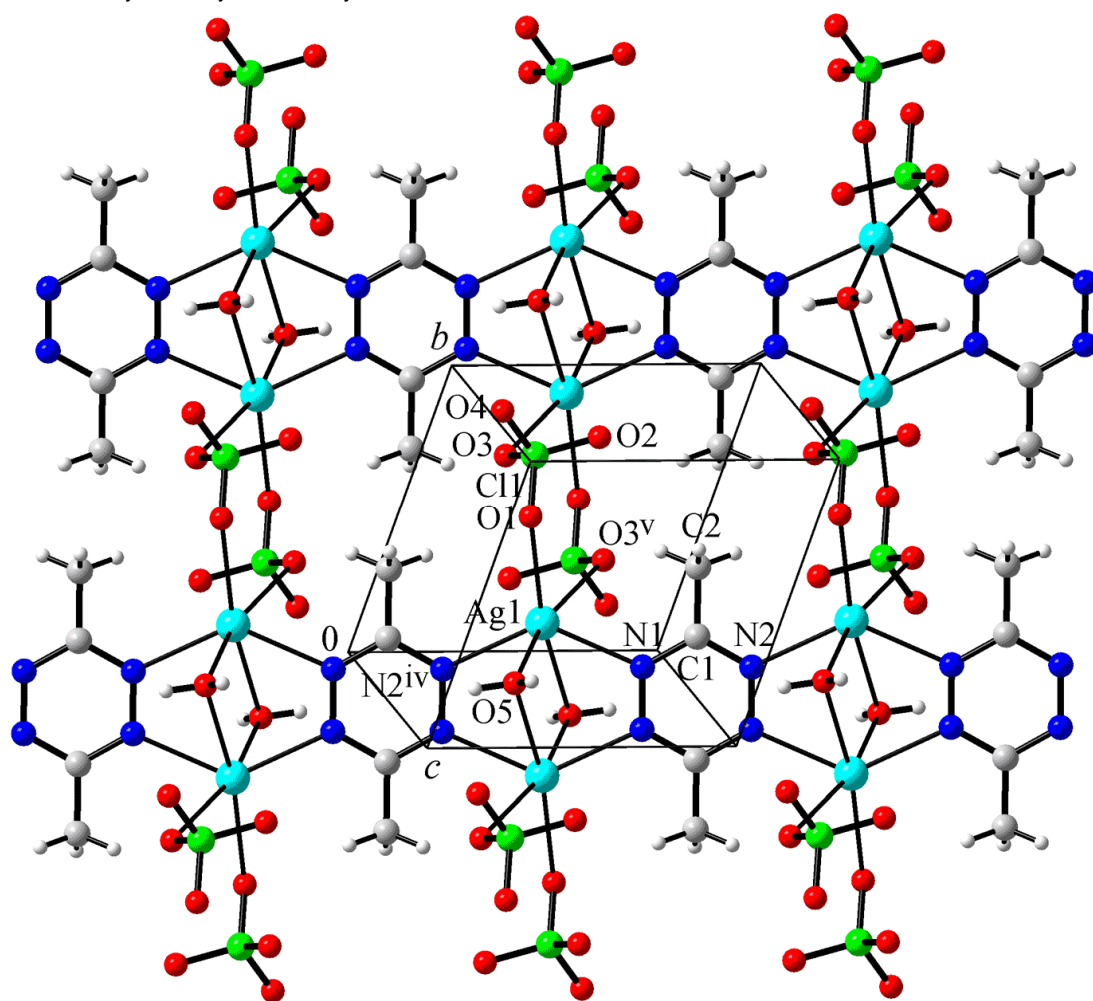


**Figure S8.** Fragment of the polymeric silver/tetrazine ribbon in the structure of **4**, showing also very close anion/ $\pi$  interaction, hydrogen bonding and bridging function of water molecules. Symmetry codes: (i)  $2-x, -y, 1-z$ ; (ii)  $1-x, -y, 1-z$ ; (iii)  $1-x, 1-y, 1-z$ ; (iv)  $-1+x, y, z$ .

**Table S1.** Geometry of the hydrogen bonding in the structure of **4**.

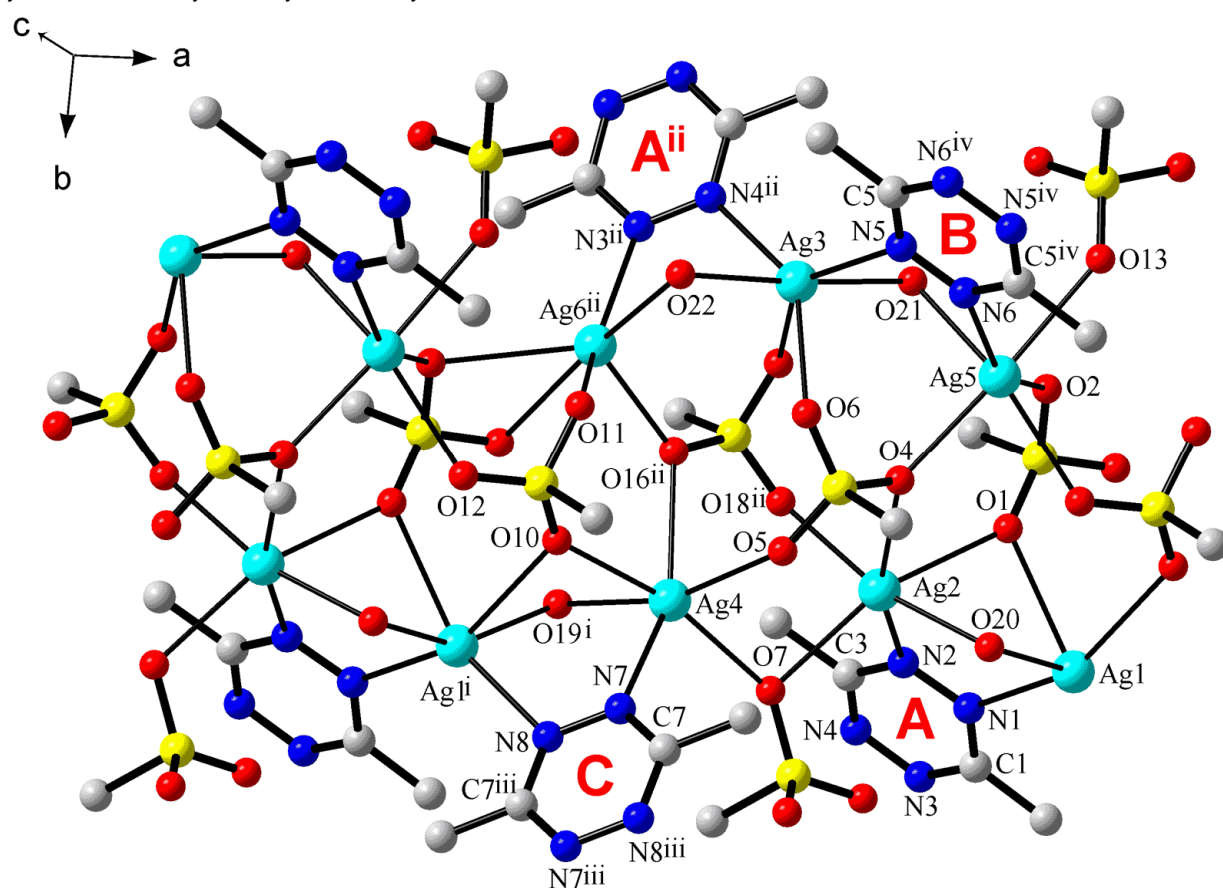
Donor	Hydrogen	Acceptor	Symmetry code	Separations, Å			$\angle$ DH---A ( $^\circ$ )
				D---A	D-H	A---H	
O5	H1W	O2	$-x+1, -y+1, -z+1$	2.948(3)	0.85	2.11	170.2
O5	H2W	O4	$-x, -y+1, -z+1$	2.972(3)	0.85	2.13	170.2



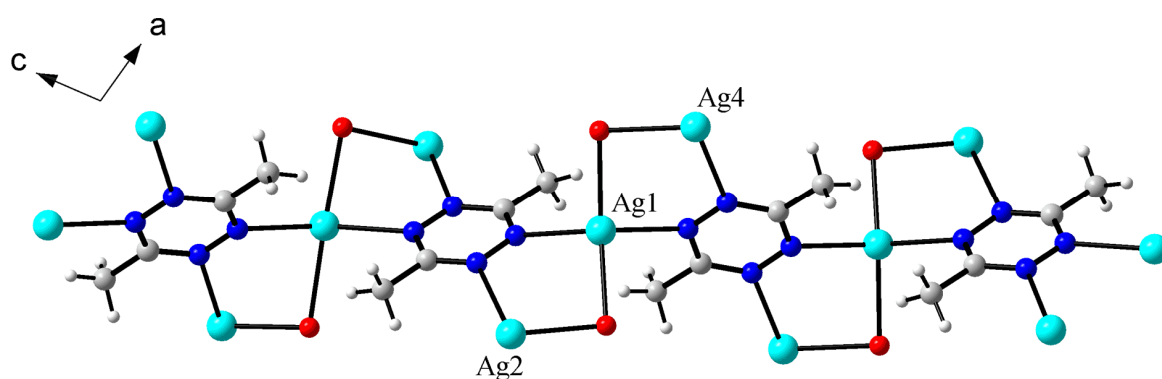


**Figure S9.** Fragment of the coordination layer in the structure of 4, showing complete coordination environment of the silver atoms. Symmetry codes: (iv)  $-1+x, y, z$ ; (v)  $1-x, 1-y, -z$ .

*Structure*  $[Ag_6(Me_2ttz)_2(H_2O)_4(CF_3SO_3)_6] 5$



**Figure S10.** Fragment of the coordination chain in the structure of **5**.  
Symmetry codes: (i)  $-1+x, y, z$ ; (ii)  $-x, -0.5+y, 0.5-z$ ; (iii)  $-1-x, 2-y, -z$ ; (iv)  $-x, 1-y, -z$ .  
The hydrogen and fluorine atoms have been omitted for clarity. Note the presence of six unique silver ions and three tetrazine molecules.



**Figure S11.** The tetrazine/silver linkage in the structure of **5**, showing also  $\mu_2$ -function of the water molecules. Each of the tetrazine ligands is tetradentate-bridging, while only 1/3 of the silver ions coordinate two tetrazine-N donors. Coordination environment of 2/3 silver ions comprises only one N-atom.