

## Silver(I) sulfate coordination polymers with 4,4'-bipyridazine and pyridazino[4,5-*d*]pyridazine

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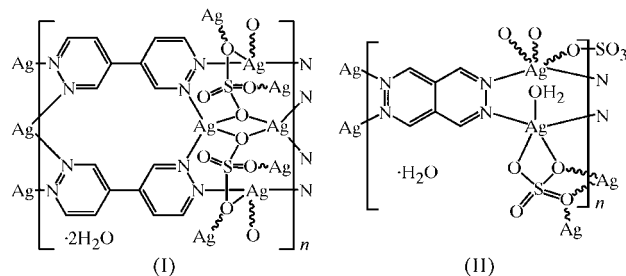
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Poly[[ $\mu_4$ -4,4'-bipyridazine- $\mu_3$ -sulfato-disilver(I)] monohydrate],  $\{[\text{Ag}_2(\text{SO}_4)(\text{C}_8\text{H}_6\text{N}_4)] \cdot \text{H}_2\text{O}\}_n$ , (I), and poly[[aqua- $\mu_4$ -pyridazino[4,5-*d*]pyridazine- $\mu_3$ -sulfato-disilver(I)] monohydrate],  $\{[\text{Ag}_2(\text{SO}_4)(\text{C}_6\text{H}_4\text{N}_4)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}\}_n$ , (II), possess three- and two-dimensional polymeric structures, respectively, supported by *N*-tetradentate coordination of the organic ligands [ $\text{Ag}-\text{N} = 2.208$  (3)– $2.384$  (3) Å] and *O*-pentadentate coordination of the sulfate anions [ $\text{Ag}-\text{O} = 2.284$  (3)– $2.700$  (2) Å]. Compound (I) is the first structurally examined complex of the new ligand 4,4'-bipyridazine; it is based upon unprecedented centrosymmetric silver–pyridazine tetramers with tetrahedral  $\text{AgN}_2\text{O}_2$  and trigonal–bipyramidal  $\text{AgN}_2\text{O}_3$  coordination of two independent  $\text{Ag}^{\text{I}}$  ions. Compound (II) adopts a typical dimeric silver–pyridazine motif incorporating two kinds of square-pyramidal  $\text{AgN}_2\text{O}_3$   $\text{Ag}^{\text{I}}$  ions. The structure exhibits short anion– $\pi$  interactions involving noncoordinated sulfate O atoms [ $\text{O} \cdots \pi = 3.041$  (3) Å].

### Comment

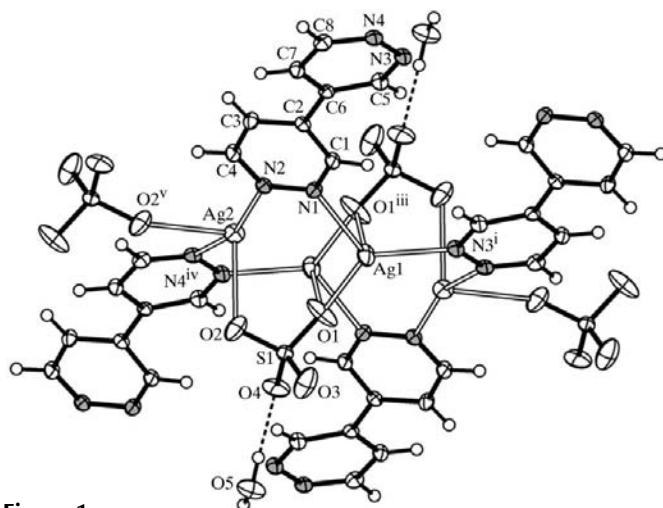
Pyridazine is an efficient bitopic N-donor ligand towards metal ions, yielding a variety of molecular, discrete polynuclear or infinite coordination patterns. Very rich and versatile possibilities for the synthesis of coordination compounds may be found for pyridazine-bridged  $\text{Cu}^{\text{I}}$  and  $\text{Ag}^{\text{I}}$  cations, the extremely soft acids favouring coordination to unsaturated N atoms (Munakata *et al.*, 1999). Many characteristic and readily predictable polynuclear (Maekawa *et al.*, 1994), chain-like or helical (Plasseraud *et al.*, 2001) copper(I) and silver(I) pyridazine motifs may be applicable for the development of complicated metal–organic frameworks as simpler subunits of the structure. Therefore, organic ligands combining multiple pyridazine donor groups provide special potential for crystal structure design. Recently, we have reported the utility of condensed pyridazines for the generation of chiral channelled

crystals (Solntsev, Sieler, Krautscheid & Domasevitch, 2004), three-dimensional arrays supporting giant cavities (Solntsev, Sieler, Chernega *et al.*, 2004) and frameworks with special anion-binding properties (Gural'skiy *et al.*, 2006). However, the chemistry of such systems is practically unexplored, although many types of pyridazines are readily available and inexpensive species. In this context, we have prepared two new silver(I) sulfate complexes with illustrative organic connectors, which combine the set of pyridazine donor functions either by coupling [4,4'-bipyridazine, compound (I)] or by annelation [pyridazino[4,5-*d*]pyridazine, compound (II)].



In compounds (I) and (II), the organic ligands utilize all available N-donor functions for coordination and act entirely as tetradentate bridges. The sulfate anions are pentadentate towards  $\text{Ag}^{\text{I}}$  ions in both structures, which has only one structural precedent, *viz.* the silver sulfate complex with 1,2-di-2-pyridylethylene (Tong *et al.*, 2002).

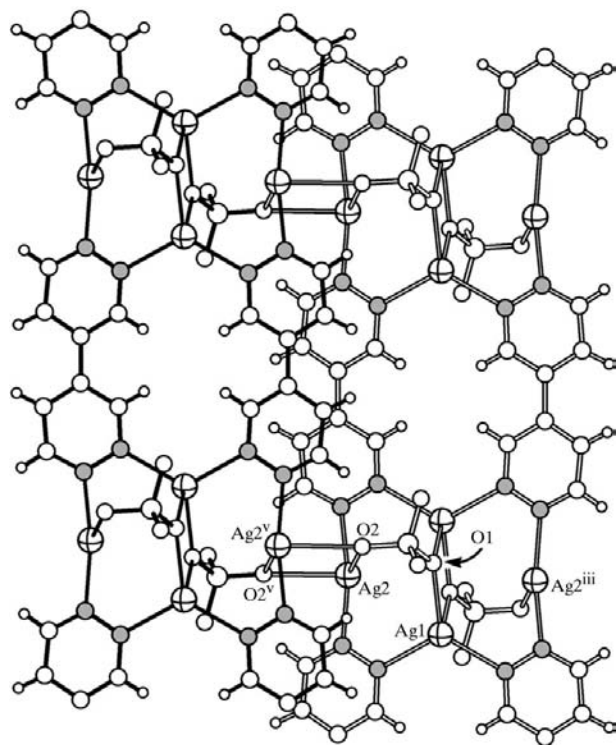
The metal–organic pattern in the 4,4'-bipyridazine complex, (I), exists as a centrosymmetric tetramer (Fig. 1), which is an unprecedented feature of silver–pyridazine systems. The fourfold nearly tetrahedral coordination environment of the  $\text{Ag}_2$  atoms is typical. It involves two short  $\text{Ag}-\text{N}$  bonds [2.208 (3) and 2.234 (3) Å] and two longer  $\text{Ag}-\text{O}$  bonds (Table 1), which are characteristic of  $\text{Ag}^{\text{I}}$  ions coordinated by a set of N,O-donor ligands (Khlobystov *et al.*, 2001). The coordination of the  $\text{Ag}^{\text{I}}$  atoms is slightly unusual: the shortest



**Figure 1**  
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 45% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i)  $-x, 1 - y, -z$ ; (iii)  $1 - x, -y, 1 - z$ ; (iv)  $1 + x, y - 1, 1 + z$ ; (v)  $1 - x, -1 - y, 1 - z$ .]

bond is Ag1–O1 [2.284 (3) Å versus Ag1–N of 2.319 (3) and 2.384 (3) Å], and two appreciably distal O atoms complete the distorted trigonal–bipyramidal environment (Table 1).

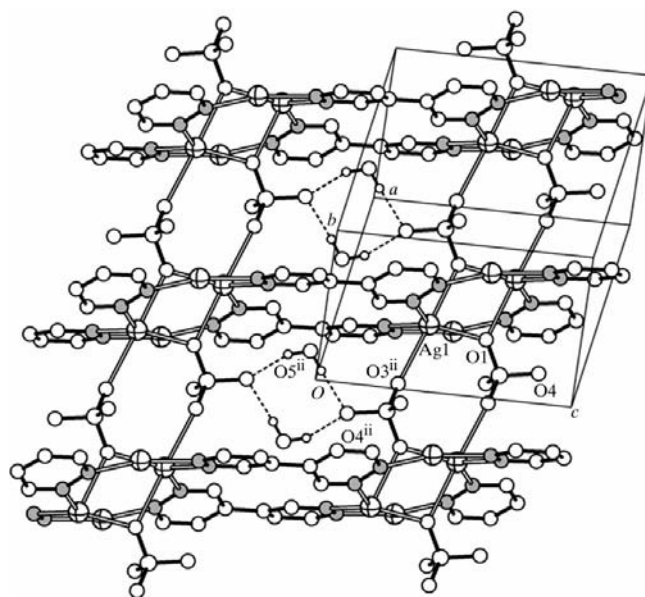
4,4′-Bipyridazine bridges connect the silver tetramers into simple chains along the [111] direction in the crystal structure (distance between the centroids of the tetramers = 11.36 Å) and further aggregation into a three-dimensional structure occurs by means of pentadentate bridging sulfate groups. Sulfate atoms O1 and O2 are coordinated to two Ag<sup>I</sup> ions [Ag1 and Ag1(1 – x, –y, 1 – z), and Ag2 and Ag2(1 – x, 1 – y, 1 – z), respectively] and they form centrosymmetric Ag<sub>2</sub>O<sub>2</sub> rhombs (Fig. 2) uniting the metal–organic chains into layers. Comparable structural functions of sulfate ions were also observed in the complex with 1,3-dithiane, with Ag–O bond lengths in the range 2.49–2.53 Å (Brammer *et al.*, 2002). Relatively distal secondary interactions connect adjacent layers [Ag1–O3(–x, –y, 1 – z) = 2.598 (3) Å] (Fig. 3). Sulfate atom O4 remains uncoordinated and is involved in strong hydrogen bonding with the solvent water molecules, which results in the formation of very typical aqua–anion dimers (Fig. 3) (Domasevitch & Boldog, 2005). Each of the available CH groups forms additional weak hydrogen bonds (Table 2), while two C1–C4/N1/N2 rings of the organic molecules [related by the symmetry operation (1 – x, –y, –z)] afford slipped  $\pi$ – $\pi$  stacking, with centroid-to-centroid and interplanar distances of 3.668 (2) and 3.323 (3) Å, respectively, and a slippage angle (angle subtended by the intercentroid vector to the plane normal) of 25.0 (2)° (Janiak, 2000).



**Figure 2**  
A view of two metal–organic chains in the structure of (I), showing the bridging function of the sulfate O atoms (O2) between the two silver–bipyridazine tetramers. [Symmetry codes: (iii) 1 – x, –y, 1 – z; (v) 1 – x, –1 – y, 1 – z.]

In the structure of compound (II), the Ag<sup>I</sup> ions and organic ligands are assembled into dimers (Fig. 4). This coordination pattern is very characteristic of pyridazines and has been observed for silver nitrate complexes with pyridazine (Carlucci *et al.*, 1998) and phthalazine (Tsuda *et al.*, 1989) and for a silver phthalate complex with phthalazine (Whitcomb & Rogers, 1997). Each of the two unique Ag<sup>I</sup> ions forms two short Ag–N bonds [2.270 (2)–2.335 (2) Å; Table 3] and the distorted square-pyramidal fivefold coordination is completed by three longer Ag–O [2.404 (2)–2.700 (2) Å] interactions with sulfate ions (Ag1), and with a sulfate ion and a water molecule (Ag2). The tetradentate bridging function of the ligands results in the formation of infinite metal–organic ribbons along the *c* axis, which are linked by pentadentate sulfate ions (Fig. 5), yielding layers parallel to the *bc* plane. Within the coordination layer, two metal–organic ribbons [related by the symmetry operation (–x, 1 – y, 1 – z)] are situated on top of one another and the ligands afford tight  $\pi$ – $\pi$  stacking (Fig. 6). This interaction occurs with an appreciably short interplanar distance of 3.369 (2) Å [centroid-to-centroid distance = 3.6791 (15) Å], but with a relatively large slippage angle of the interacting groups [23.7 (2)°], which is typical for slipped  $\pi$ – $\pi$  contacts of electron-deficient heteroaromatic rings (Janiak, 2000).

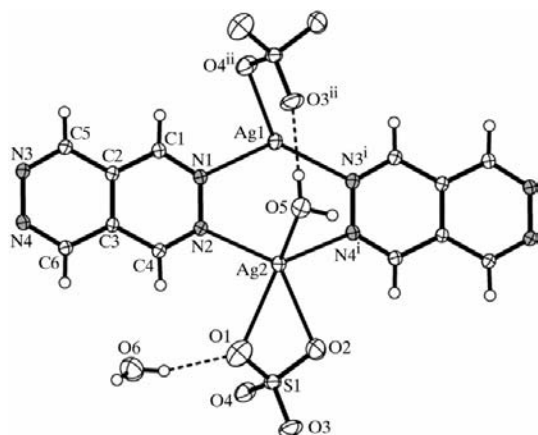
Adjacent layers, which are related by translation along the *a* axis, are held together by hydrogen bonding involving the sulfate ions and coordinated (O5) and noncoordinated (O6) water molecules. One of these hydrogen bonds is three-centred (Table 4 and Fig. 6). Within the set of weak interlayer forces, however, the most notable interaction is a very unusual stacking between the aromatic  $\pi$ -cloud (atoms N3/N4/C6/C3/C2/C5) and sulfate atom O3(1 – x, 1 – y, 1 – z) [group centroid  $\cdots$ O distance = 3.041 (3) Å; angle of the O  $\cdots$   $\pi$  axis to the plane of the aromatic cycle = 82.8 (1)°]. A slightly shorter



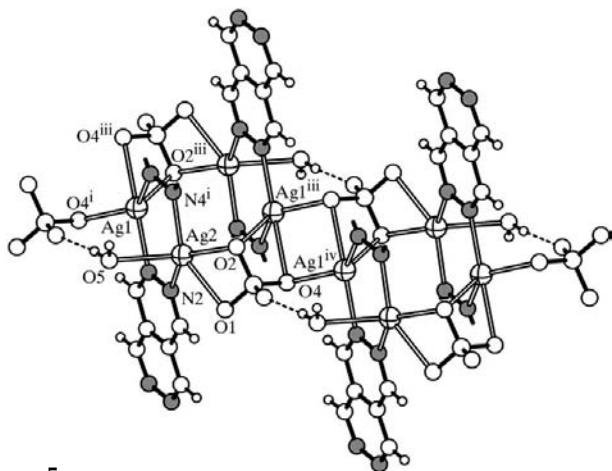
**Figure 3**  
The interconnection of the silver–pyridazine tetramers in the structure of (I) via Ag1–O3<sup>ii</sup> coordination bonds and hydrogen bonding with solvent water molecules. [Symmetry code: (ii) –x, –y, 1 – z.]

contact of this type was also observed in the zinc(II) and copper(II) nitrate complexes ( $O \cdots \pi = 2.83$  and  $2.87$  Å, respectively; Gural'skiy *et al.*, 2006). Such close and directional interaction with a negatively polarized atom clearly reflects the pronounced electron-deficient character of the ligand. Indeed, the bicyclic system of pyridazine rings sharing their *d* edge even exhibits appreciable azadiene reactivity similar to 1,2,4,5-tetrazine (Haider, 1991). The parameters for the close anion- $\pi$  interaction in (II) are comparable with those observed for most electron-deficient systems, such as 1,3,5-triazines (Maheswari *et al.*, 2006) and 1,2,4,5-tetrazines (Schottel *et al.*, 2006) [ $F(O) \cdots \pi = 2.80$ – $3.20$  Å].

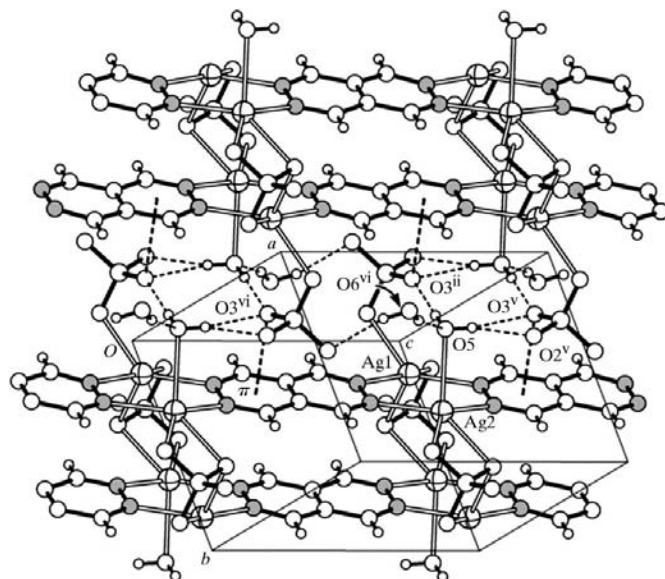
It is worth noting that compound (I) displays no anion- $\pi$  interactions. This may be attributed to the significantly higher lowest unoccupied molecular orbital energy of the pyridazine system compared with pyridazino[4,5-*d*]pyridazine ( $-0.288$  and  $-1.591$  eV, respectively; Haider, 1991). The structure of the organic ligands in (I) and (II) reveals a somewhat lower



**Figure 4**  
The structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i)  $x, y, 1 + z$ ; (ii)  $x, y - 1, z$ .]



**Figure 5**  
The coordination environment of the two unique Ag ions and the pentadentate bridging function of the sulfate ions in the structure of (II). [Symmetry codes: (i)  $x, y, 1 + z$ ; (ii)  $x, y - 1, z$ ; (iii)  $-x, 1 - y, 2 - z$ ; (iv)  $x, 1 + y, z$ .]



**Figure 6**  
Interlayer interactions in the structure of (II), showing the hydrogen-bonding scheme with coordinated (O5) and noncoordinated (O6) water molecules, and the close anion- $\pi$  interactions of the noncoordinated sulfate O atoms (O3). [Symmetry codes: (ii)  $x, y - 1, z$ ; (v)  $1 - x, 1 - y, 2 - z$ ; (vi)  $1 - x, 1 - y, 1 - z$ .]

delocalization of  $\pi$ -electron density within the frame of condensed pyridazine and an appreciable contribution of the bis(azadiene) resonance structure (*e.g.*  $-C=N-N=C-$ ). Thus, the N–N bonds in the molecule of pyridazino[4,5-*d*]pyridazine are longer than in 4,4'-bipyridazine [ $1.375$  (3) and  $1.379$  (3) Å *versus*  $1.348$  (4) and  $1.350$  (4) Å], while all C–N bond lengths are shorter [ $1.305$  (3)– $1.308$  (3) Å *versus*  $1.324$  (4)– $1.332$  (4) Å]. Coordination to many metal ions is also of importance for the electronic structure of the ligand, since in noncoordinated pyridazino[4,5-*d*]pyridazine, the C–N bonds are certainly longer (1.310 and 1.314 Å; Sabelli *et al.*, 1969).

In the molecule of 4,4'-bipyridazine, the C2–C6 bond [ $1.479$  (4) Å] between the rings is characteristic of a single bond between two  $Csp^2$  atoms and this indicates a lack of conjugation between the pyridazine rings. The molecule is not planar and possesses a slightly twisted conformation, with a dihedral angle between the two pyridazine rings of  $22.3$  (3)° [torsion angle C3–C2–C6–C7 =  $22.7$  (5)°]. The pyridazine rings adopt a *cis* configuration, which is important for the organization of simpler metal–organic chains instead of the four-connected network.

In conclusion, either condensed pyridazino[4,5-*d*]pyridazine or 4,4'-bipyridazine reveal a maximal tetradentate function towards  $Ag^I$  ions, even in combination with nucleophilic sulfate counteranions. The structures reported in this paper could provide attractive prototypes for the design of solid-state architecture using 'double pyridazine' ligands.

## Experimental

Pyridazino[4,5-*d*]pyridazine was prepared with 1,2,4,5-tetrazine as starting material, in accordance with the literature method of

Gural'skiy *et al.* (2006). For the preparation of (I), solid silver sulfate (0.062 g, 0.1 mmol) was added to a solution of 4,4'-bipyridazine (0.032 g, 0.2 mmol) in water (3 ml). The mixture was allowed to stand for 7–8 d until total dissolution of Ag<sub>2</sub>SO<sub>4</sub> was observed, which was accompanied by crystallization of complex (I) as yellow prisms (yield 0.078 g, 80%). In the same manner, compound (II) (yellow blocks) was synthesized in 70% yield starting with a solution of pyridazino[4,5-*d*]pyridazine (0.026 g, 0.2 mmol) in water (3 ml).

**Compound (I)**

*Crystal data*

[Ag<sub>2</sub>(SO<sub>4</sub>)(C<sub>8</sub>H<sub>4</sub>N<sub>4</sub>)]·H<sub>2</sub>O  
*M<sub>r</sub>* = 487.98  
 Triclinic, *P* $\bar{1}$   
*a* = 7.4829 (9) Å  
*b* = 8.4881 (10) Å  
*c* = 10.9267 (10) Å  
 $\alpha$  = 67.172 (9)°  
 $\beta$  = 88.971 (8)°

*Data collection*

Siemens SMART CCD area-detector diffractometer  
 Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.514, *T<sub>max</sub>* = 0.609

*Refinement*

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.028  
*wR*(*F*<sup>2</sup>) = 0.073  
*S* = 1.05  
 2629 reflections  
 181 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 1.17 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.98 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °) for (I).

Ag1—O1	2.284 (3)	Ag2—N2	2.208 (3)
Ag1—N3 <sup>i</sup>	2.319 (3)	Ag2—N4 <sup>iv</sup>	2.234 (3)
Ag1—N1	2.385 (3)	Ag2—O2	2.495 (3)
Ag1—O3 <sup>ii</sup>	2.598 (3)	Ag2—O2 <sup>v</sup>	2.672 (3)
Ag1—O1 <sup>iii</sup>	2.680 (3)		
O1—Ag1—N3 <sup>i</sup>	125.75 (13)	O3 <sup>ii</sup> —Ag1—O1 <sup>iii</sup>	174.71 (11)
O1—Ag1—N1	115.15 (13)	N2—Ag2—N4 <sup>iv</sup>	160.29 (10)
N3 <sup>i</sup> —Ag1—N1	118.59 (9)	N2—Ag2—O2	112.90 (11)
O1—Ag1—O3 <sup>ii</sup>	106.76 (13)	N4 <sup>iv</sup> —Ag2—O2	85.79 (10)
O1—Ag1—O1 <sup>iii</sup>	73.57 (12)	N2—Ag2—O2 <sup>v</sup>	86.93 (10)
N3 <sup>i</sup> —Ag1—O1 <sup>iii</sup>	97.76 (11)	N4 <sup>iv</sup> —Ag2—O2 <sup>v</sup>	86.32 (10)
N1—Ag1—O1 <sup>iii</sup>	91.52 (11)	O2—Ag2—O2 <sup>v</sup>	91.57 (9)

Symmetry codes: (i)  $-x, -y + 1, -z$ ; (ii)  $-x, -y, -z + 1$ ; (iii)  $-x + 1, -y, -z + 1$ ; (iv)  $x + 1, y - 1, z + 1$ ; (v)  $-x + 1, -y - 1, -z + 1$ .

**Table 2**

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H1W...O4	0.85	1.89	2.737 (4)	177
O5—H2W...O4 <sup>vi</sup>	0.85	1.99	2.773 (4)	152
C1—H1...O5 <sup>ii</sup>	0.96	2.40	3.210 (5)	142
C3—H3...O4 <sup>vii</sup>	0.96	2.39	3.334 (4)	169
C4—H4...O4 <sup>v</sup>	0.96	2.58	3.462 (5)	153
C5—H5...O5 <sup>viii</sup>	0.96	2.46	3.395 (5)	166
C7—H7...O3 <sup>viii</sup>	0.96	2.33	3.120 (4)	139
C8—H8...O2 <sup>ix</sup>	0.96	2.43	3.164 (5)	133

Symmetry codes: (ii)  $-x, -y, -z + 1$ ; (v)  $-x + 1, -y - 1, -z + 1$ ; (vi)  $-x + 1, -y - 1, -z + 2$ ; (vii)  $x, y, z - 1$ ; (viii)  $x, y + 1, z - 1$ ; (ix)  $-x, -y, -z$ .

**Compound (II)**

*Crystal data*

[Ag<sub>2</sub>(SO<sub>4</sub>)(C<sub>6</sub>H<sub>4</sub>N<sub>4</sub>)(H<sub>2</sub>O)]·H<sub>2</sub>O  
*M<sub>r</sub>* = 479.96  
 Triclinic, *P* $\bar{1}$   
*a* = 8.3733 (2) Å  
*b* = 8.7790 (2) Å  
*c* = 8.9006 (3) Å  
 $\alpha$  = 85.9270 (10)°  
 $\beta$  = 74.334 (2)°  
 $\gamma$  = 68.8160 (10)°  
*V* = 587.14 (3) Å<sup>3</sup>  
*Z* = 2  
 Mo *K*α radiation  
 $\mu$  = 3.54 mm<sup>-1</sup>  
*T* = 273 (2) K  
 0.40 × 0.20 × 0.10 mm

*Data collection*

Siemens SMART CCD area-detector diffractometer  
 Absorption correction: empirical (using intensity measurements) (*SADABS*; Sheldrick, 1996)  
*T<sub>min</sub>* = 0.325, *T<sub>max</sub>* = 0.704  
 6007 measured reflections  
 3014 independent reflections  
 2720 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.018

*Refinement*

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.022  
*wR*(*F*<sup>2</sup>) = 0.054  
*S* = 1.04  
 3014 reflections  
 173 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.84 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$

**Table 3**

Selected geometric parameters (Å, °) for (II).

Ag1—N3 <sup>i</sup>	2.295 (2)	Ag2—N2	2.2703 (19)
Ag1—N1	2.335 (2)	Ag2—N4 <sup>i</sup>	2.2890 (19)
Ag1—O4 <sup>ii</sup>	2.403 (2)	Ag2—O2	2.551 (4)
Ag1—O2 <sup>iii</sup>	2.632 (3)	Ag2—O5	2.600 (2)
Ag1—O4 <sup>iii</sup>	2.700 (2)	Ag2—O1	2.621 (3)
N3 <sup>i</sup> —Ag1—N1	126.39 (7)	N2—Ag2—N4 <sup>i</sup>	130.29 (7)
N3 <sup>i</sup> —Ag1—O4 <sup>ii</sup>	133.04 (7)	N2—Ag2—O2	136.82 (7)
N1—Ag1—O4 <sup>ii</sup>	84.30 (8)	N4 <sup>i</sup> —Ag2—O2	83.34 (8)
N3 <sup>i</sup> —Ag1—O2 <sup>iii</sup>	105.18 (9)	N2—Ag2—O5	85.30 (7)
N1—Ag1—O2 <sup>iii</sup>	104.87 (8)	O2—Ag2—O5	129.78 (8)
O4 <sup>ii</sup> —Ag1—O2 <sup>iii</sup>	97.94 (9)	N2—Ag2—O1	89.94 (8)
N3 <sup>i</sup> —Ag1—O4 <sup>iii</sup>	81.48 (7)	N4 <sup>i</sup> —Ag2—O1	137.17 (8)
N1—Ag1—O4 <sup>iii</sup>	150.62 (7)	O2—Ag2—O1	54.11 (8)
O2 <sup>iii</sup> —Ag1—O4 <sup>iii</sup>	52.93 (7)	O5—Ag2—O1	117.25 (7)

Symmetry codes: (i)  $x, y, z + 1$ ; (ii)  $x, y - 1, z$ ; (iii)  $-x, -y + 1, -z + 2$ .

**Table 4**

Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O5—H1W...O3 <sup>ii</sup>	0.85	1.94	2.785 (3)	173
O5—H2W...O3 <sup>iv</sup>	0.85	2.19	2.985 (4)	156
O5—H2W...O2 <sup>iv</sup>	0.85	2.39	3.104 (4)	142
O6—H3W...O1	0.85	2.09	2.914 (4)	164
O6—H4W...O5 <sup>v</sup>	0.85	1.96	2.792 (3)	167
C4—H4...O6	0.96	2.46	3.260 (4)	141

Symmetry codes: (ii)  $x, y - 1, z$ ; (iv)  $-x + 1, -y + 1, -z + 2$ ; (v)  $-x + 1, -y + 1, -z + 1$ .

H atoms were placed in geometrically idealized positions and treated as riding, with O—H = 0.85 Å and C—H = 0.96 Å, and with *U*<sub>iso</sub>(H) = 1.2*U*<sub>eq</sub>(C) or 1.5*U*<sub>eq</sub>(O).

For both compounds, data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SAINT-NT* (Bruker, 1999); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Version 1.700.00; Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3101). Services for accessing these data are described at the back of the journal.

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