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# A grid-like two-dimensional Ag$^{I}$ coordination polymer: poly[[[$\mu_3$-*N*′-(4-cyanobenzylidene)isonicotinohydrazide]silver(I)] perchlorate]

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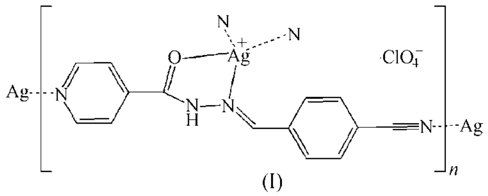
This study presents new coordinating modes of a Schiff base with three coordinating groups and an interesting two-dimensional framework based on two types of constructing units. In the title compound, $\{[Ag(C_{14}H_{10}N_4O)]ClO_4\}_n$, the Ag$^{I}$ ion is coordinated by three N atoms and one O atom from three different *N*′-(4-cyanobenzylidene)isonicotinohydrazide (*L*) ligands, forming a primary distorted square-planar coordination geometry. Two ligands each bridge two metal centres through one carbonitrile N atom in a monodentate mode and the hydrazide N and O atoms in a bidentate mode to form a small centrosymmetric (2+2)-$Ag_2L_2$ ring as a principal constructing unit. The pyridyl N atoms from four ligands in four of these small rings coordinate to Ag atoms in adjacent rings to form a large hexanuclear silver grid. A two-dimensional framework of rectangular grids is constructed from these small rings and large grids. Two perchlorate anions are located in each large grid and are bound to the grid by N—H···O hydrogen bonding. Crosslinking between the layers is achieved through long Ag···O interactions between the perchlorate anions and Ag atoms in adjacent layers.

## Comment

Silver coordination polymers have been studied widely not only for their utility in special functional materials, but also for their fascinating structures derived from variable coordination numbers (from 2 to 6) of Ag atoms and different conformations around silver metal centres (Sumby & Hardie, 2005; Dong *et al.*, 2004). Multiple pyridyl, carbonitrile or pyridyl–carbonitrile ligands are good bridging organic ligands in coordination interactions with Ag atoms (Antonioli *et al.*, 2006; Bourlier *et al.*, 2007).

Carbonitrile and pyridyl N atoms in the same organic ligand possess different coordinating properties. Taking advantage of these differences, chemists can design and construct novel silver metal–organic frameworks (Fernandez-Fernandez *et al.*, 2006; Niu *et al.*, 2007; Gonzalez *et al.*, 2002). On the other hand, hydrazide groups in some organic ligands have been widely used as five-atom-ring chelates with some transition metal atoms, such as Cu, Co and Zn (Iskander *et al.*, 2001; Qiu *et al.*, 2006; Gao *et al.*, 2004). This group should coordinate in a bidentate fashion to Ag atoms. However, there are no reports in the literature concerning complexes derived from these components. We report here the structure of a two-dimensional silver coordination polymer, (I), of the bridging ligand *N*′-(4-cyanobenzylidene)isonicotinohydrazide, which contains carbonitrile, pyridyl and hydrazide groups. The variety of potential coordinating atoms in this ligand allows it to be used as a $\mu_2$- or $\mu_3$-bridging or a monodentate ligand.



(I)

In (I), the central silver ion is coordinated by one O atom and one N atom (O1 and N3) from the hydrazide chain and by the pyridyl and carbonitrile N atoms of two other ligands [N1$^{ii}$ and N4$^{i}$; symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; Fig. 1]. Hydrazide atoms O1 and N3 are coordinated to the silver ion in a bidentate coordinating mode to form a planar five-membered chelate ring (Ag1/N3/N2/C6/

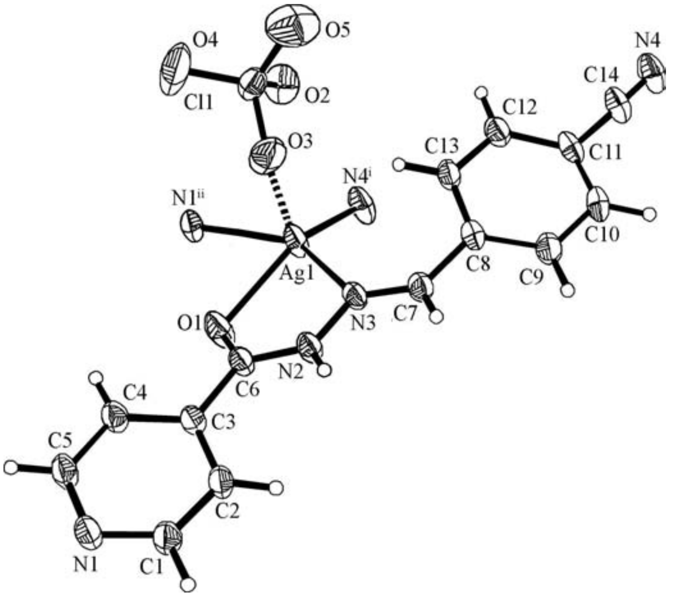


**Figure 1**
A view of the Ag$^{I}$ coordination environment in the polymeric structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.]

O1), in which the maximum deviation from the plane is 0.010 (3) Å for atom O1. The coordination geometry about atom Ag1 is distorted square planar, with the distortion arising primarily from the bite angle imposed by the chelating hydrazide group. The length of the Ag—N bond involving the hydrazide N atom is about 0.1 Å longer than those involving the pyridyl and carbonitrile N atoms (Table 1). As is to be expected from the bite angle formed by the coordination of the hydrazide group, the geometry of this part of the ligand in (I) differs slightly from that of the free ligand (de Souza *et al.*, 2007).

In (I), the *N*′-(4-cyanobenzylidene)isonicotinohydrazide ($L$) ligand acts as a $\mu_3$-bridging ligand. Two ligands each bridge two Ag atoms through one carbonitrile N atom in a monodentate mode, and the hydrazide N and O atoms in a bidentate mode, to form a small centrosymmetric (2+2)-$Ag_2L_2$ ring. The Ag···Ag separation in one ring is 9.316 (3) Å. Four of these rings are linked to each other by pyridyl atom N1, coordinating to Ag atoms in adjacent small rings to produce a large rectangular grid with Ag atoms at the corners of the rectangle. The large grid contains six Ag atoms (Fig. 2). Adjacent Ag atoms along the long side of the rectangle are bridged by the entire length of a ligand *via* the pyridyl and carbonitrile N atoms to give an Ag···Ag separation of 18.237 (3) Å. The short side of the rectangle involves two Ag atoms bridged *via* the bidentate hydrazide O1 and N3 atoms and the monodentate pyridyl N1 atom to give an Ag···Ag separation of 9.696 (3) Å. Two perchlorate counter-anions are located in the centrosymmetric nano-sized grid and interact with the rim of the rectangular grid through N—H···O hydrogen bonds, which involve the amine group of the ligand (N2) and atom O2 of a counter-anion (Table 2). As there is an Ag atom in the middle of each long side of the rectangular grid, and this Ag atom is also a corner of an adjacent rectangle, a brickwork lattice of two-dimensional layers is formed (Fig. 3). The layers lie approximately parallel to the (103) plane.

It is noteworthy that parallel two-dimensional layers stack together to form a nanometre-scale one-dimensional tunnel along the *a* axis. These nanotunnels are filled with perchlorate counter-anions. Thus, the crystals of (I) potentially have the ability to undergo ion-exchange from perchlorate anions to other analogues such as $BF_4^-$. In addition to the above-mentioned hydrogen bonding between counter-anions and the ligands of the layer in which the counter-anions are located, there are weak Ag···O interactions between atoms O2 and O3 of one counter-anion and an Ag atom in a neighbouring layer, with Ag···O separations of 2.968 (3) and 3.016 (3) Å. Weak inter-layer $\pi$–$\pi$ stacking, occurring between the benzene and pyridyl rings from neighbouring layers with a centroid-to-centroid distance of about 4 Å, also contribute somewhat to the supramolecular three-dimensional structure of (I).

The structures of some related silver(I)–pyridyl coordination polymers with perchlorate anions acting as both counter-anions and coordinating ligands have been reported. They are ({$Ag_2$[1,3-bis(4,5-dihydro-1*H*-imidazol-2-yl)benzene]$_2$}-$(ClO_4)_2)_n$ (Ren *et al.*, 2004), {[Ag(2,4′-bipyridine)]$ClO_4$}$_n$ (Tong *et al.*, 1998), [Ag(di-2-pyridyl ketone)$ClO_4$]$_n$ (Yang *et al.*, 2000) and {$Ag_{2.5}$[2,5-bis(2-benzodiazine)-3,4-diaza-2,4-hexadiene]$_{1.5}(ClO_4)_{2.5}(H_2O)_2$}$_n$ (Dong *et al.*, 2005). The coordination mode of the perchlorate anions with the silver metal centre in the first of these compounds is very similar to that observed in (I). The silver ion has weak contacts with two O atoms from one perchlorate anion, with Ag···O separations of 2.83 and 3.11 Å. Another similarity is that the perchlorate anion forms weak hydrogen-bonding interactions with the uncoordinated N atoms from the organic ligand, with N···O ($D$···$A$) distances of 3.04 and 3.08 Å, which are longer than that in (I) (Ren *et al.*, 2004). In the other three cited silver coordination polymers, the perchlorate O atoms are directly coordinated to the silver metal centres with Ag—O bond lengths less than 2.7 Å. Unlike the weak Ag···O contacts present in (I) and ({$Ag_2$[1,3-bis(4,5-dihydro-1*H*-imidazol-2-yl)benzene]$_2$}$(ClO_4)_2)_n$, which involve two O atoms of the anion, these strong Ag—O contacts form between just one perchlorate O atom and one Ag atom.

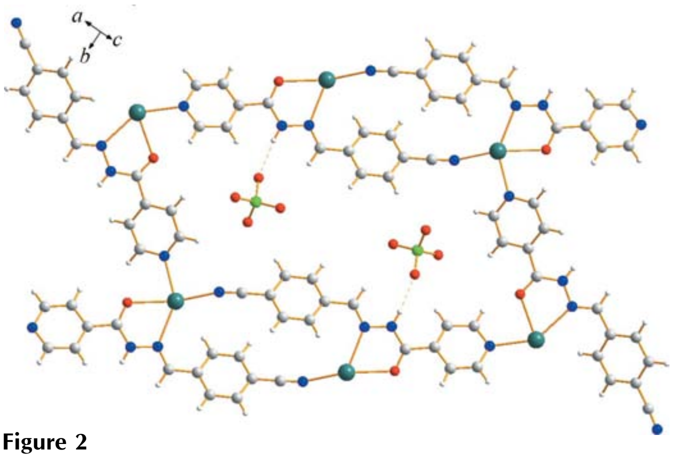


**Figure 2**
The octanuclear silver grid surrounding two counter-anions (dashed lines represent hydrogen bonds).

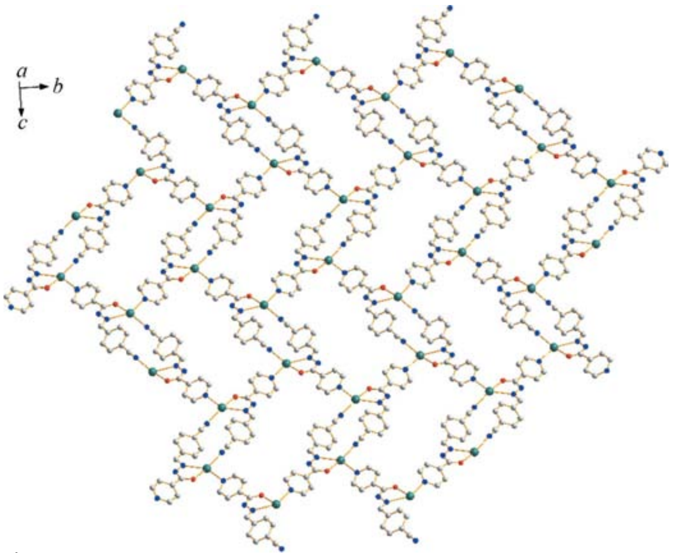


**Figure 3**
The two-dimensional layers in (I). All counter-anions and H atoms have been omitted for clarity.

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## Experimental

A solution of $AgClO_4 \cdot H_2O$ (0.023 g, 0.1 mmol) in methanol (10 ml) was carefully layered on a methanol/chloroform solution (5 ml/10 ml) of $N'$-(4-cyanobenzylidene)isonicotinohydrazide (0.025 g, 0.1 mmol) in a straight glass tube. About 10 d later, colourless single crystals of (I) suitable for X-ray analysis were obtained (yield 43%). Elemental analysis calculated for $C_{14}H_{10}AgClN_4O_5$: C 36.75, H 2.20, N 12.24%; found: C 36.86, H 2.11, N 12.09%.

*Crystal data*

$[Ag(C_{14}H_{10}N_4O)]ClO_4$
$M_r = 457.58$
Monoclinic, $P2_1/n$
$a = 8.5763$ (5) Å
$b = 13.4913$ (8) Å
$c = 14.1944$ (8) Å
$\beta = 103.370$ (1)°
$V = 1597.86$ (16) Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.46$ mm$^{-1}$
$T = 173$ (2) K
0.46 × 0.34 × 0.32 mm

*Data collection*

Siemens SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.552$, $T_{max} = 0.652$
8730 measured reflections
2979 independent reflections
2637 reflections with $I > 2\sigma(I)$
$R_{int} = 0.012$

*Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.069$
$S = 1.00$
2979 reflections
230 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.52$ e Å$^{-3}$
$\Delta\rho_{min} = -0.43$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ag1—N4$^{i}$ | 2.336 (3) | Ag1—O1 | 2.4501 (19) |
| Ag1—N1$^{ii}$ | 2.366 (2) | Ag1—N3 | 2.462 (2) |
| | | | |
| N4$^{i}$—Ag1—N1$^{ii}$ | 94.11 (10) | N4$^{i}$—Ag1—N3 | 120.32 (9) |
| N4$^{i}$—Ag1—O1 | 153.07 (10) | N1$^{ii}$—Ag1—N3 | 144.64 (7) |
| N1$^{ii}$—Ag1—O1 | 79.15 (7) | O1—Ag1—N3 | 66.51 (6) |

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x-\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$.

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H14···O2$^{iii}$ | 0.850 (18) | 2.15 (2) | 2.956 (3) | 159 (3) |

Symmetry code: (iii) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

C-bound H atoms were placed in calculated positions and refined using a riding model [C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. The N-bound H atom was first introduced in a calculated position, and then its position and displacement parameter were refined with the N—H bond distance restrained to 0.88 (2) Å. The final difference Fourier map had a highest peak at 0.94 Å from atom Ag1 and a deepest hole at 0.71 Å from atom Cl1, but was otherwise featureless.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3107). Services for accessing these data are described at the back of the journal.

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