

## Poly[bis( $\mu_2$ -2-aminopyrazine- $\kappa^2N^1:N^4$ )-( $\mu_2$ -nitrate- $\kappa^2O:O$ )(nitrate- $\kappa^2O,O'$ )-disilver(I)]: an achiral two-dimensional coordination polymer forming chiral crystals

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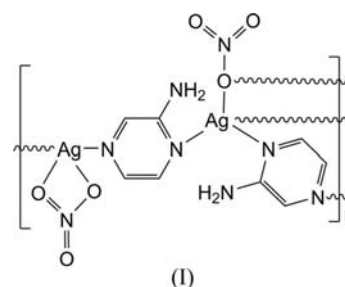
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The solution reaction of  $\text{AgNO}_3$  and 2-aminopyrazine (apyz) in a 1:1 ratio gives rise to the title compound,  $[\text{Ag}_2(\text{NO}_3)_2(\text{C}_4\text{H}_5\text{N}_3)_2]_n$  (I), which possesses a chiral crystal structure. In (I), both of the crystallographically independent  $\text{Ag}^{\text{I}}$  cations are coordinated in tetrahedral geometries by two N atoms from two apyz ligands and two O atoms from nitrate anions; however, the  $\text{Ag}^{\text{I}}$  centers show two different coordination environments in which one is coordinated by two O atoms from two different symmetry-related nitrate anions and the second is coordinated by two O atoms from a single nitrate anion. The crystal structure consists of one-dimensional  $\text{Ag}^{\text{I}}$ -apyz chains, which are further extended by  $\mu_2$ - $\kappa^2O:O$  nitrate anions into a two-dimensional (4,4) sheet.  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{C}_{\text{apyz}}-\text{H}\cdots\text{O}$  hydrogen bonds connect neighboring sheets to form a three-dimensional supramolecular framework.

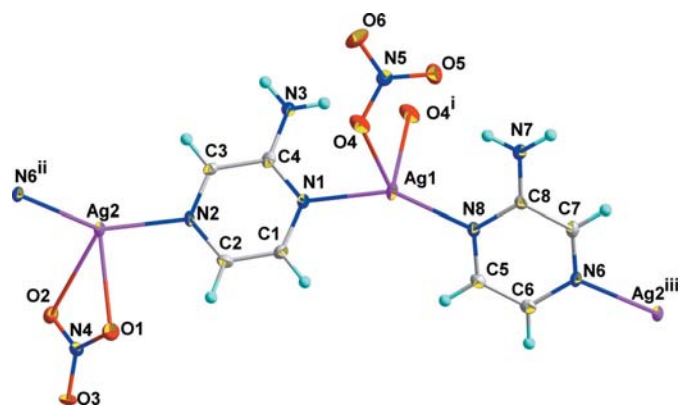
### Comment

Interest in crystal engineering and supramolecular chemistry is rapidly increasing because of the diverse and aesthetic structural topologies of the products of such studies and their potential use in optical, electrical, catalytic and gas storage applications and even in drug delivery (Blake, Brooks *et al.*, 1999; Blake, Champness *et al.*, 1999; Blake *et al.*, 1997; Evans & Lin, 2002; Kitagawa *et al.*, 2004; Yaghi *et al.*, 2003; Applegarth *et al.*, 2005). In particular, there is considerable interest in chiral solid-state materials, owing to their potential applications in asymmetric catalysis and chiral separation (Kesanli & Lin, 2003; Pidcock, 2005). Although these chiral materials can be synthesized from chiral organic spacers and metal ions (Dai *et al.*, 2005; Wang *et al.*, 2008; Zaworotko, 2001), compounds presenting chiral crystal structures self-assembled from the

$\text{Ag}^{\text{I}}$  cation and achiral 2-aminopyrazine (apyz) ligand have not been documented yet. Recently, we have undertaken a series of investigations into the self-assembly of the  $\text{Ag}^{\text{I}}$  cation with different angular and linear bipodal *N*-donor ligands, such as aminopyrimidine and aminopyrazine (*e.g.* Luo, Huang, Chen *et al.*, 2008; Luo, Huang, Zhang *et al.*, 2008; Luo, Sun, Xu *et al.*, 2009; Luo, Sun, Zhang, Huang & Zheng, 2009; Luo, Sun, Zhang, Xu *et al.*, 2009; Sun, Luo, Huang *et al.*, 2009; Sun, Luo, Xu *et al.*, 2009; Sun, Luo, Zhang *et al.*, 2009), with the principal aim of obtaining supramolecular compounds or multifunctional coordination polymers. During an attempt to exploit the influence of anions on the  $\text{Ag}^{\text{I}}$ -apyz system, we surprisingly obtained the title achiral coordination polymer, (I), which stacks to give a chiral crystal structure.

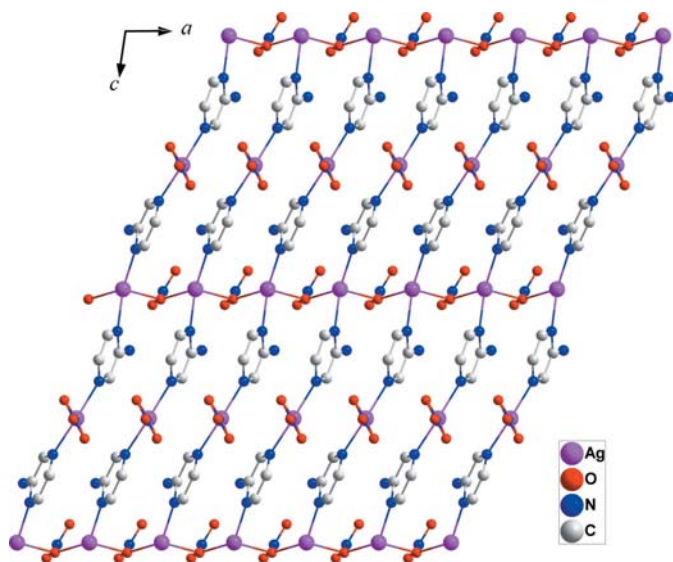


The asymmetric unit of (I) contains two different  $\text{Ag}^{\text{I}}$  cations, two apyz ligands and two nitrate anions. The coordination geometry of the  $\text{Ag}^{\text{I}}$  cation is tetrahedral, and each  $\text{Ag}^{\text{I}}$  cation is coordinated by two N atoms from two different apyz ligands and two O atoms from nitrate anions (Fig. 1); however, the  $\text{Ag}^{\text{I}}$  centers show two different coordination environments in which  $\text{Ag}^{\text{I}}$  is coordinated by two O atoms from two different symmetry-related nitrate anions and  $\text{Ag}^{\text{II}}$  is coordinated by two O atoms from a single nitrate anion. The nitrate anions show two different coordination modes, namely  $\mu_2$ - $\kappa^2O:O$  and  $\kappa^2O,O'$ , which are found in many other silver(I) compounds (Cui & He, 2003; Faure *et al.*, 1985; Chen *et al.*, 2004). The geometric parameters, especially the bond angles

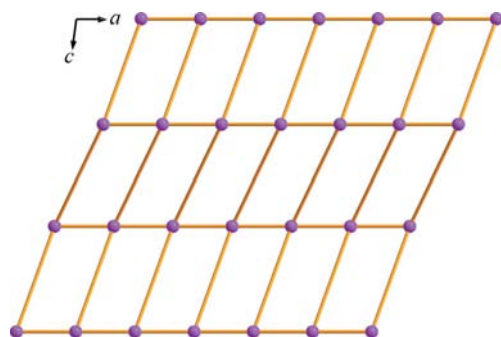


**Figure 1**  
The structure of (I), showing the atom-numbering scheme and the coordination environment around the  $\text{Ag}^{\text{I}}$  centers. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $x - 1, y, z + 1$ ; (iii)  $x + 1, y, z - 1$ .]

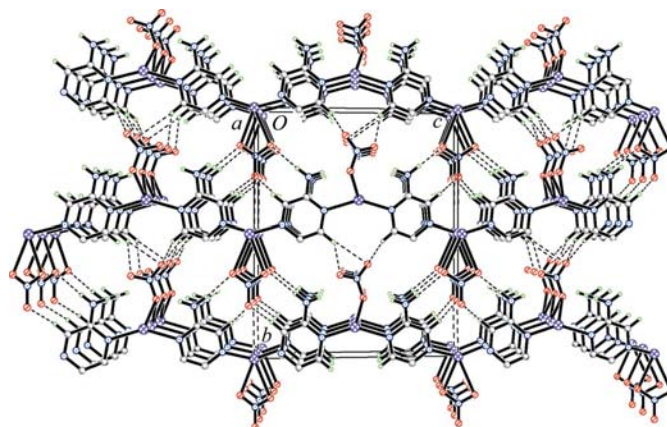
around Ag1 and Ag2, are obviously different. The bond angles around Ag1 and Ag2 open up from the ideal tetrahedral angle to 145.84 (14) and 150.84 (14)°, respectively, while the remaining angles around Ag1 and Ag2 are in the ranges 85.20 (12)–125.32 (12) and 49.89 (9)–113.25 (12)°, respectively. The Ag–N and Ag–O bond lengths (Table 1) are comparable to those in related compounds (Fan *et al.*, 2007; Oxtoby *et al.*, 2002; Turner *et al.*, 2005; Massoud & Langer, 2009; Massoud *et al.*, 2009; Withersby *et al.*, 1997; Zartilas *et al.*, 2007). There are also weak Ag···C interactions with Ag···C distances in the range 3.314 (4)–3.322 (4) Å, which fall in the secondary bonding range (the sum of the van der Waals radii of Ag and C is 3.42 Å; Mascall *et al.*, 2000). Some polymeric silver(I) compounds of aromatic ligands have been reported to present similar Ag···C interactions, with Ag···C bond distances of *ca* 2.80–3.38 Å (Blake *et al.*, 2000; Khlobystov *et al.*, 2001). Therefore, these interactions in (I) are very important, in the present case, for the packing of (I) in the solid state. Between neighboring chains, the shortest Ag···Ag separation is 3.6087 (6) Å, which is longer than twice the van der Waals radius of Ag<sup>I</sup> (1.72 Å; Bondi, 1964), indicating no direct metal–metal interaction.



**Figure 2**  
A ball-stick perspective view, along the *b* axis, of the two-dimensional sheet in (I). H atoms have been omitted for clarity.



**Figure 3**  
A schematic view, along the *b* axis, of the (4,4)-net in (I).



**Figure 4**  
A perspective view, along the *a* axis, of the three-dimensional supra-molecular framework incorporating N—H···O and C—H···O hydrogen bonds (dashed lines).

The apyz ligand acts in a  $\mu_2$ -*N,N'*-bidentate fashion to link Ag<sup>I</sup> cations to form a one-dimensional chain along the *c* axis in which Ag1 and Ag2 alternate. The  $\mu_2$ - $\kappa^2$ O-nitrate anions play an important role in constructing the two-dimensional undulating sheet (Fig. 2) in which  $\mu_2$ - $\kappa^2$ O-nitrate anions bridge neighboring chains. Fig. 3 shows a schematic depiction of the sheet, which has a (4,4) topology (Batten & Robson, 1998), with Ag<sup>I</sup> cations as the four-connected nodes and with meshes of dimensions 3.61 × 7.13 Å. In addition, amino groups from apyz ligands act as hydrogen-bond donors with N···O distances in the range 2.912 (5)–3.099 (5) Å (Table 2) to form intra-sheet N—H···O hydrogen bonds. Apyz–nitrate C—H···O hydrogen bonds with C···O distances in the range 3.066 (5)–3.521 (5) Å not only support the N—H···O hydrogen bonds within the sheets but also link the sheets to form a three-dimensional network (Fig. 4).

## Experimental

All reagents and solvents were used as obtained commercially without further purification. To an aqueous solution (14 ml) of AgNO<sub>3</sub> (170 mg, 1.0 mmol), aminopyrazine (95 mg, 1.0 mmol) in ethanol (12 ml) was added dropwise under continuous stirring. The resulting grey precipitate was filtered off, and the clear filtrate was left undisturbed for two weeks. Yellow block-shaped crystals suitable for X-ray measurements formed, were collected by filtration and dried in air; the yield was 62% with respect to the ligand. Analysis calculated for C<sub>8</sub>H<sub>10</sub>Ag<sub>2</sub>N<sub>8</sub>O<sub>6</sub>: C 18.13, H 1.90, N 21.14%; found: C 18.18, H 1.81, N 21.21%. IR (KBr, cm<sup>-1</sup>): 3332 (*s, br*), 3142 (*s, br*), 1643 (*vs*), 1582 (*vs*), 1530 (*s*), 1475 (*sh*), 1207 (*m*), 1038 (*w*), 1001 (*m*), 828 (*m*), 619 (*w*), 431 (*w*).

### Crystal data

[Ag<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>5</sub>N<sub>3</sub>)<sub>2</sub>]  
*M<sub>r</sub>* = 529.98  
 Monoclinic, *P*2<sub>1</sub>  
*a* = 3.6087 (1) Å  
*b* = 15.4328 (5) Å  
*c* = 12.7326 (3) Å  
 $\beta$  = 97.566 (2)°

*V* = 702.93 (3) Å<sup>3</sup>  
*Z* = 2  
 Mo K $\alpha$  radiation  
 $\mu$  = 2.84 mm<sup>-1</sup>  
*T* = 123 K  
 0.18 × 0.15 × 0.12 mm

## Data collection

Oxford Diffraction Gemini S Ultra diffractometer	3805 measured reflections
Absorption correction: multi-scan ( <i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	2573 independent reflections
$T_{\min} = 0.629$ , $T_{\max} = 0.727$	2436 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.034$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	H-atom parameters constrained
$wR(F^2) = 0.050$	$\Delta\rho_{\text{max}} = 0.61 \text{ e } \text{\AA}^{-3}$
$S = 0.99$	$\Delta\rho_{\text{min}} = -0.72 \text{ e } \text{\AA}^{-3}$
2573 reflections	Absolute structure: Flack (1983),
217 parameters	812 Friedel pairs
1 restraint	Flack parameter: 0.01 (3)

All H atoms were positioned geometrically and treated as riding [C—H = 0.95 Å and N—H = 0.88 Å, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ ].

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; structure solution: *SHELXS97* (Sheldrick, 2008); structure refinement: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3128). Services for accessing these data are described at the back of the journal.

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**Table 1**

Selected geometric parameters (Å, °).

Ag1—N1	2.214 (3)	Ag2—N2	2.224 (3)
Ag1—N8	2.176 (3)	Ag2—N6 <sup>ii</sup>	2.234 (3)
Ag1—O4	2.463 (3)	Ag2—O1	2.555 (3)
Ag1—O4 <sup>i</sup>	2.577 (3)	Ag2—O2	2.581 (3)
N1—Ag1—N8	145.84 (14)	N2—Ag2—O2	117.70 (12)
N1—Ag1—O4	85.20 (12)	N6 <sup>ii</sup> —Ag2—O1	113.25 (12)
N1—Ag1—O4 <sup>i</sup>	95.44 (11)	N6 <sup>ii</sup> —Ag2—O2	90.22 (12)
N8—Ag1—O4	125.32 (12)	O1—Ag2—O2	49.89 (9)
N8—Ag1—O4 <sup>i</sup>	98.35 (12)	O4—Ag1—O4 <sup>i</sup>	91.43 (12)
N2—Ag2—N6 <sup>ii</sup>	150.84 (14)	N5—O4—Ag1 <sup>iii</sup>	128.4 (2)
N2—Ag2—O1	92.56 (12)	C7—N6—Ag2 <sup>iv</sup>	120.4 (3)

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

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N7—H7B <sup>..</sup> ·O5	0.88	2.08	2.912 (5)	157
N3—H3B <sup>..</sup> ·O4 <sup>i</sup>	0.88	2.17	2.998 (5)	156
N3—H3C <sup>..</sup> ·O2 <sup>v</sup>	0.88	2.23	3.099 (5)	172
N7—H7C <sup>..</sup> ·O1 <sup>vi</sup>	0.88	2.19	3.031 (5)	161
C1—H1A <sup>..</sup> ·O5 <sup>vii</sup>	0.95	2.49	3.211 (5)	133
C1—H1A <sup>..</sup> ·O6 <sup>viii</sup>	0.95	2.57	3.521 (6)	175
C5—H5A <sup>..</sup> ·O6 <sup>viii</sup>	0.95	2.44	3.108 (6)	127
C5—H5A <sup>..</sup> ·O6 <sup>vii</sup>	0.95	2.55	3.299 (6)	136
C3—H3A <sup>..</sup> ·O3 <sup>ix</sup>	0.95	2.34	3.066 (5)	133
C6—H6A <sup>..</sup> ·O2 <sup>iv</sup>	0.95	2.56	3.266 (5)	131
C7—H7A <sup>..</sup> ·O3 <sup>x</sup>	0.95	2.31	3.109 (5)	142

Symmetry codes: (i)  $x + 1, y, z$ ; (iv)  $x + 1, y, z - 1$ ; (v)  $-x + 1, y - \frac{1}{2}, -z + 2$ ; (vi)  $-x, y - \frac{1}{2}, -z + 1$ ; (vii)  $-x, y + \frac{1}{2}, -z + 1$ ; (viii)  $-x + 1, y + \frac{1}{2}, -z + 1$ ; (ix)  $-x, y - \frac{1}{2}, -z + 2$ ; (x)  $-x + 1, y - \frac{1}{2}, -z + 1$ .

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