

Bis[4-(dimethylamino)pyridine- κ N¹]-silver(I) nitrate dihydrate

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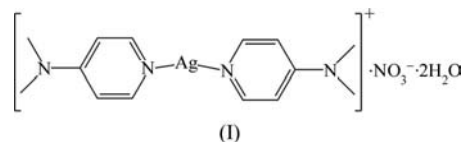
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The title compound, [Ag(C₇H₁₀N₂)₂]NO₃·2H₂O or [Ag(dmap)₂]⁺NO₃⁻·2H₂O, where dmap is 4-(dimethylamino)pyridine, has a distorted linear coordination geometry around the Ag^I ion. A novel pattern of water–nitrate hydrogen-bonded anionic strands is formed in the *c* direction, with the cationic [Ag(dmap)₂]⁺ monomers trapped between them. The Ag^I ion and the nitrate group atoms, as well as the water molecules (including the H atoms), are on a crystallographic mirror plane (Wyckoff position 4*a*). The influence of bulky methyl substituents in position 4 of the 4-(dimethylamino)pyridine ligand on packing is discussed. The absolute structure was determined unequivocally.

Comment

Aminopyridines are water-soluble ligands which attract an intense interest owing to their versatile coordination modes, especially with Ag^I ions (Bowmaker *et al.*, 2005). This type of ligand can coordinate to the metal center either *via* the ring N atom alone (as a monodentate ligand) or *via* both the ring N atom and the amine group N atom (as bridging and/or bidentate ligand). When 2-aminopyridine (2-ampy) reacts with AgNO₃ in water/ethanol solution, three compounds are formed with different stoichiometric ratios, namely [Ag(2-ampy)₂]NO₃ (Fun *et al.*, 2008), [Ag(2-ampy)₃]NO₃ and [Ag₃(NO₃)₂(2-ampy)₄]NO₃ (Bowmaker *et al.*, 2005). In the case of 3- and 4-aminopyridine, only one compound is known for each, *viz.* {[Ag₄(NO₃)₄(3-ampy)₄]_n} and [Ag(4-ampy)₂]NO₃ (Abu-Youssef *et al.*, 2006*a,b*). In all the previously mentioned compounds, N–H···O hydrogen bonds are formed between the amine groups of the ligands and nitrate O atoms. We have prepared the title silver(I) compound, (I), with 4-(dimethylamino)pyridine (dmap) as a continuation of our previous work on Ag^I compounds with pyridine-type ligands and especially aminopyridines (Abu-Youssef *et al.*, 2006*a,b*, 2007).

The molecular structure of (I) is shown in Fig. 1. The Ag^I ion is bonded to two dmap ligands *via* their pyridine N atoms, forming a distorted linear coordination geometry, which is the most preferred coordination geometry for Ag^I ions (Abu-Youssef *et al.*, 2007; Massoud & Langer, 2009). Table 2 shows a comparison between (I) and some related aminopyridine–Ag^I compounds. Shorter Ag–N bond distances, wider N–Ag–N angles and hence weaker Ag···O interactions are reported for



the related linear compounds [Ag(dmap)₂]PF₆ (Lin *et al.*, 2008), [Ag(4-ampy)₂]NO₃ (Abu-Youssef *et al.*, 2006*a*) and [Ag(2-ampy)₂]NO₃ (Fun *et al.*, 2008) compared with those found in (I), while for the trigonal-planar and tetrahedral compounds [Ag₃(NO₃)₂(2-ampy)₄]NO₃ (Bowmaker *et al.*, 2005) and {[Ag₄(NO₃)₄(3-ampy)₄]_n} (Abu-Youssef *et al.*, 2006*b*), longer Ag–N bond distances and narrower N–Ag–N angles are found. In the case of [Ag(dmap)₂]PF₆ (Lin *et al.*, 2008), no interaction could be considered between the PF₆⁻ and Ag^I ions, the shortest Ag···F distances being 3.007 (3) and 3.528 (6) Å.

The novel system of strong water/nitrate hydrogen bonds in (I) is shown in Fig. 2, with data in Table 1. The water/nitrate hydrogen bonds form rings [with graph-set symbol R₃²(12); Bernstein *et al.*, 1995], leading to anionic strands propagating in the *c* direction. The [Ag(dmap)₂]⁺ units are arranged in an

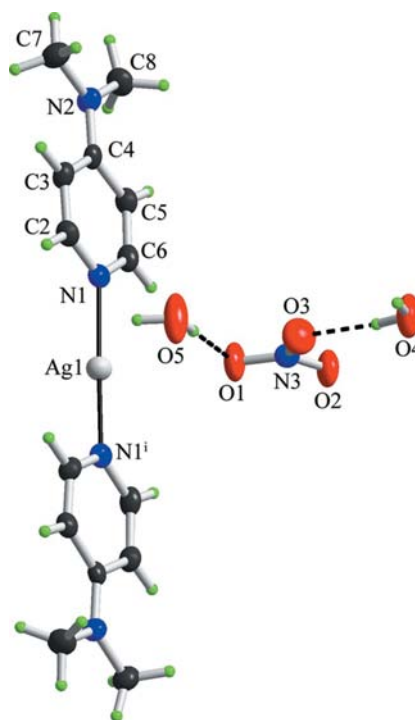


Figure 1
The atomic numbering scheme for (I), with atomic displacement ellipsoids drawn at the 50% probability level; broken lines indicate hydrogen bonds (see Table 1). [Symmetry code: (i) $-x + 2, y, z$.]

alternating zigzag pattern between these hydrogen-bonded strands. The water/nitrate strands are also arranged in an alternating pattern above one another, with no interaction found between the successive strands. The packing scheme for (I) is shown in Fig. 3. A weak C—H...O hydrogen bond (Table 1) is found between one of the methyl groups of the dmap ligand and one of the nitrate O atoms.

No π – π interactions were found in (I), following the requirement stated by Janiak (2000).

Introducing the two methyl groups as substituents on the amine N atom of the 4-aminopyridine ligand has greatly affected the structural features of the resulting compound. The bulky terminal groups of the ligand in (I) force both the nitrate anions and the water molecules to be arranged around the metal centers and not to be packed in between the $[\text{Ag}(\text{dmap})_2]^+$ units as in the case of $[\text{Ag}(\text{4-ampy})_2]\text{NO}_3$ (Abu-Youssef *et al.*, 2006a). Nitrate anions are known for their ability to form strong hydrogen bonds, being better acceptors than hexafluorophosphate anions in the case of $[\text{Ag}(\text{dmap})_2]\text{-PF}_6$ (Lin *et al.*, 2008). In addition to the steric effect of the dmap ligand and the presence of nitrate groups as counterions, the high water content increases the possibility of the

formation of hydrogen bonds, with the nitrate groups engaging in novel water/nitrate hydrogen-bonded strands. This structure is evidently very stable, since different crystal morphologies were formed, which in all cases afforded the same internal order.

Experimental

To an aqueous solution (4 ml) of AgNO_3 (0.169 g, 1 mmol), an ethanol solution (4 ml) of 4-(dimethylamino)pyridine (0.367 g, 1 mmol) was added. Drops of 0.1 M HNO_3 were added and a brown precipitate formed, which was dissolved by stirring and heating. The final clear solution was allowed to stand for 4 d, after which time colorless crystals of different morphologies (needles, prisms, plates and cubes) suitable for X-ray measurements were collected and dried in air, with a yield of 50% with respect to the metal. Note that all the crystals have the same structure as confirmed by X-ray single-crystal analysis. The reported determination was carried out on a crystal which formed as a prism.

Crystal data

$[\text{Ag}(\text{C}_7\text{H}_{10}\text{N}_2)_2]\text{NO}_3 \cdot 2\text{H}_2\text{O}$	$V = 1817.22 (15) \text{ \AA}^3$
$M_r = 450.25$	$Z = 4$
Orthorhombic, $Cmc2_1$	Mo $K\alpha$ radiation
$a = 20.3572 (10) \text{ \AA}$	$\mu = 1.14 \text{ mm}^{-1}$
$b = 11.3133 (5) \text{ \AA}$	$T = 153 \text{ K}$
$c = 7.8904 (4) \text{ \AA}$	$0.32 \times 0.17 \times 0.14 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer	14780 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2003)	2856 independent reflections
$T_{\min} = 0.711$, $T_{\max} = 0.856$	2268 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.062$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$	$\Delta\rho_{\text{max}} = 0.74 \text{ e \AA}^{-3}$
$wR(F^2) = 0.064$	$\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$
$S = 1.00$	Absolute structure: Flack (1983),
2856 reflections	1330 Friedel pairs
137 parameters	Flack parameter: $-0.06 (3)$
5 restraints	
H atoms treated by a mixture of independent and constrained refinement	

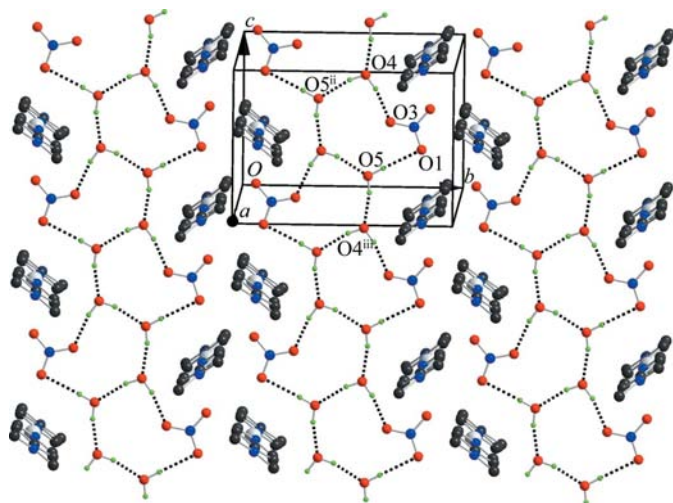


Figure 2

A perspective view of (I), showing the water/nitrate hydrogen-bonded strands running in the c direction and the zigzag arrangement of $[\text{Ag}(\text{dmap})_2]^+$ ions. See Table 1 for symmetry codes.

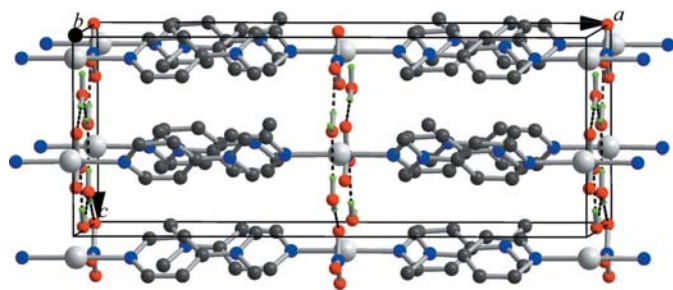


Figure 3

A packing diagram for (I); broken lines indicate hydrogen bonds. Note that no interaction is found between the ligands, and the water/nitrate strands run around the Ag^+ centers.

Table 1

Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
$\text{O4—H41}\cdots\text{O3}$	0.88 (2)	1.88 (3)	2.746 (6)	168 (8)
$\text{O4—H42}\cdots\text{O5}^{\text{ii}}$	0.853 (19)	1.88 (2)	2.719 (6)	167 (6)
$\text{O5—H51}\cdots\text{O4}^{\text{iii}}$	0.86 (2)	1.84 (2)	2.690 (8)	166 (6)
$\text{O5—H52}\cdots\text{O1}$	0.882 (19)	2.19 (2)	3.074 (6)	179 (6)
$\text{O5—H52}\cdots\text{O3}$	0.882 (19)	2.41 (5)	3.003 (6)	125 (5)
$\text{C7—H7B}\cdots\text{O3}^{\text{iv}}$	0.98	2.62	3.452 (3)	143

Symmetry codes: (ii) $-x + 2, -y + 1, z + \frac{1}{2}$; (iii) $x, y, z - 1$; (iv) $-x + \frac{3}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$.

Aromatic H atoms were refined isotropically, with $U_{\text{iso}}(\text{H})$ values set at $1.2U_{\text{eq}}(\text{C})$, and their positions were constrained to an ideal geometry using an appropriate riding model ($\text{C—H} = 0.95 \text{ \AA}$). For methyl groups, N—C—H angles (109.5°) were kept fixed, while the torsion angle was allowed to refine with the starting positions based on the circular Fourier synthesis averaged using the local threefold

Table 2

Comparison of Ag–N bond lengths (Å), N–Ag–N angles (°) and Ag···O interactions (Å) in some related silver(I) aminopyridine compounds.

Compound	Ag–N	N–Ag–N	Ag···O
[Ag(dmap) ₂][NO ₃ ·2H ₂ O, (I)]	2.1589 (18)	170.68 (10)	2.683 (4) 2.770 (5)
[Ag(dmap) ₂][PF ₆ ^a]	2.119 (3)	180	–
[Ag(4-ampy) ₂][NO ₃ ^b]	2.125 (6)	173.07 (2)	2.889 (6)
[Ag ₄ (NO ₃) ₄ (3-ampy) ₄] _n ^c	2.216 (2)	124.98 (10)	2.445 (3)
	2.228 (2)	126.32 (10)	2.562 (3)
	2.297 (2)	140.07 (8)	2.643 (2)
	2.340 (2)		2.463 (2)
	2.317 (2)		2.456 (3)
	2.369 (3)		2.570 (2)
	2.207 (2)		2.582 (2)
[Ag ₃ (NO ₃) ₂ (2-ampy) ₄][NO ₃] ^d	2.198 (3)	154.122 (11)	2.539 (3)
	2.186 (3)	82.617 (12)	2.786 (3)
	2.384 (3)		
	2.419 (3)		
[Ag(2-ampy) ₃][NO ₃] ^d	2.222 (17)	105.05 (7)	2.696 (2)
	2.232 (19)	113.18 (7)	
	2.396 (2)	140.64 (6)	
[Ag(2-ampy) ₂][NO ₃] ^e	2.1406 (14)	175.97 (6)	2.849 (3)
	2.1413 (14)	180	
	2.1115 (14)		

References: (a) Lin *et al.* (2008); (b) Abu-Youssef *et al.* (2006a); (c) Abu-Youssef *et al.* (2006b); (d) Bowmaker *et al.* (2005); (e) Fun *et al.* (2008).

axis. A common $U_{\text{iso}}(\text{H})$ value was refined for the methyl H atoms [final value = 0.059 (4) Å²] and a constrained C–H distance of 0.98 Å was applied. Water H atoms were restrained to have O–H distances of 0.88 (2) Å, with a common $U_{\text{iso}}(\text{H})$ refined [final value = 0.070 (10) Å²].

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINTE* (Bruker, 2003); data reduction: *SAINTE* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick,

2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3107). Services for accessing these data are described at the back of the journal.

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