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Bis(4-aminopyridine)silver(I) nitrate and tris(2,6-diaminopyridine)silver(I) nitrate

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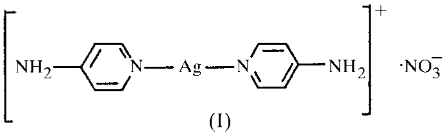
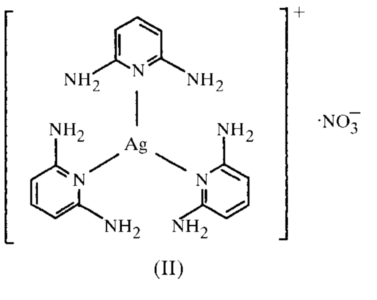
The bis(4-aminopyridine)silver(I) cation in $[Ag(C_5H_6N_2)_2]NO_3$ has the Ag atom on a twofold axis and displays an N—Ag—N angle of 174.43 (15)° and an Ag—N distance of 2.122 (3) Å. The two ligands are planar and the angle between the two ligand planes is 79.45 (9)°. The pyridine rings are stacked in piles with an interplanar distance of 3.614 (5) Å, a distance that strongly suggests that pyridine π–π interactions have an appreciable importance with respect to the non-bonded crystal organization. The tris(2,6-diaminopyridine)silver(I) cation in $[Ag(C_5H_7N_3)_3]NO_3$ has Ag—N distances of 2.243 (2), 2.2613 (17) and 2.4278 (18) Å, and N—Ag—N angles of 114.33 (7), 134.91 (7) and 114.33 (7)°. The Ag^+ ion is situated 0.1531 (2) Å from the plane defined by the three pyridine N atoms.

Comment

Silver is an often used metal in the construction of coordination polymers and related supramolecular systems with multidentate pyridine derivatives (Aakeroy *et al.*, 1998; Wu *et al.*, 1999, and references therein). The silver(I) ion exhibits a large flexibility in its coordination with nitrogen-containing aromatic ligands, with coordination numbers ranging from two to eight. The geometries of the complexes are, however, usually determined by the coordination requirements of the multidentate ligands. With monodentate pyridine or functionalized pyridine ligands, virtually linear complexes are the most



(I)



(II)

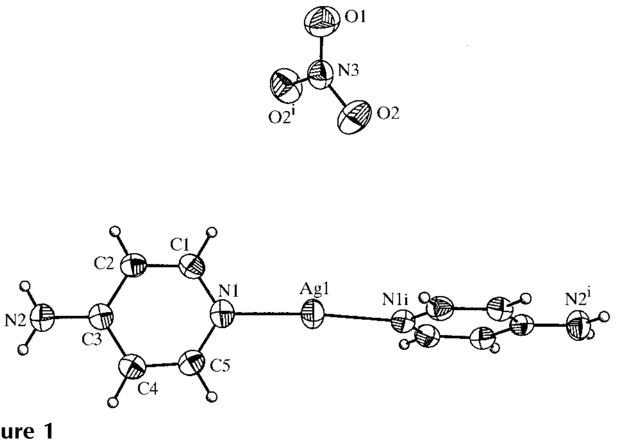


Figure 1
The molecular structure of bis(4-aminopyridine)silver(I) nitrate, (I). Displacement ellipsoids are shown at the 30% probability level for non-H atoms. [Symmetry code: (i) $-x, y, \frac{1}{2} - z$.]

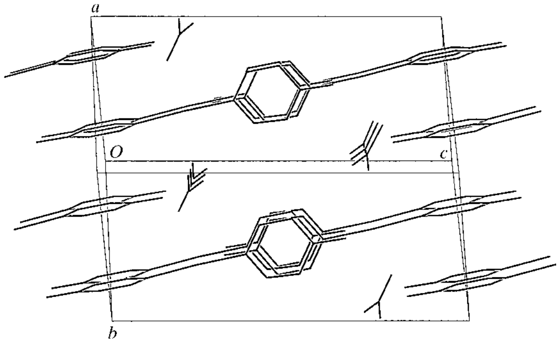


Figure 2
View perpendicular to the *c* axis of the packing of bis(4-aminopyridine)silver(I) nitrate, (I), in the unit cell.

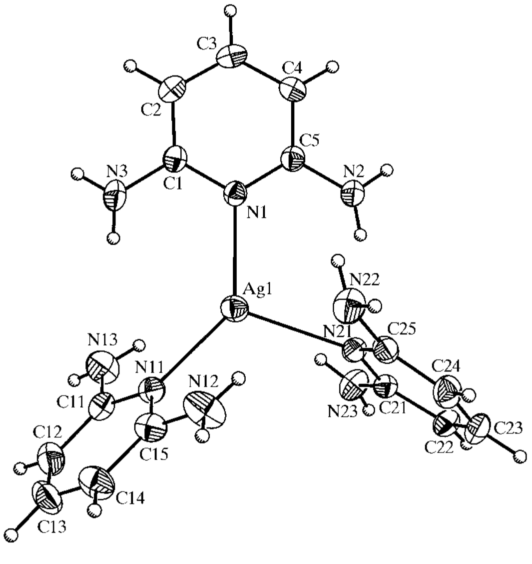


Figure 3
Molecular structure of the tris(2,6-diaminopyridine)silver(I) cation of (II). Displacement ellipsoids are shown at the 30% probability level for non-H atoms.

frequently encountered. For the two-coordinate complexes so far structurally characterized, the average values of the N—Ag—N angles and Ag—N distances are 169 (9)° and 2.167 (17) Å, respectively (Allen & Kennard, 1993). Exceptions from two-coordinate complexes are the tris(isonicotinamide)silver(I) cation with a nearly trigonal geometry (Aakeroy *et al.*, 1998) and the tetrahedral tetrapyridinesilver(I) cation (Nilsson & Oskarsson, 1982; Dyason *et al.*, 1985). In this contribution, we wish to present the crystal structures of silver(I) complexes with 4-aminopyridine and 2,6-diaminopyridine ligands, namely the title complexes (I) and (II).

The bis(4-aminopyridine)silver(I) cation (Fig. 1) has an N1—Ag1—N1^{i} angle of 174.43 (15)° and an Ag1—N1 distance of 2.122 (3) Å. The 4-aminopyridine ligands are planar with a mean deviation from the plane defined by the seven non-H atoms of 0.008 (2) Å. The angle between the planes defined by the two ligands is 79.45 (9)°. The hydrogen bonds formed between the amino group and the nitrate anions are weak, with N···O distances of 2.963 (4) and 3.189 (5) Å. The packing is shown in Fig. 2. Viewed perpendicular to the *c* axis, the pyridine rings are seen to be stacked into piles. The interplanar distance between the 4-aminopyridine ligands in a pile is 3.614 (5) Å, a distance that strongly suggests that pyridine π–π interactions play an appreciably important role in the non-bonded crystal organization (*e.g.* Kiralj *et al.*, 1999; Ishow *et al.*, 1998; Wu *et al.*, 1999; Yoshida *et al.*, 1998).

In tris(2,6-diaminopyridine)silver(I) nitrate, the Ag$^+$ ion is coordinated by three 2,6-diaminopyridine ligands, with Ag—N distances of 2.243 (2), 2.2613 (17) and 2.4278 (18) Å in a distorted trigonal geometry (Fig. 3). The N1—Ag—N11, N11—Ag1—N21 and N21—Ag1—N1 angles are 114.33 (7), 134.91 (7) and 114.33 (7)°, respectively. The Ag$^+$ ion is situated 0.1531 (2) Å from the plane defined by the N1, N11 and N21 atoms. These values can be compared with those of the tris(isonicotinamide)silver(I) cation, in which the Ag—N distances range from 2.213 (2) to 2.321 (2) Å (Aakeroy *et al.*, 1998). The geometry of the ligand remains virtually unchanged upon coordination with the Ag$^+$ cation as compared with the geometry of the 2,6-diaminopyridinium cation (Kristiansson, 1999). Eight of the 12 amino H atoms participate in hydrogen bonds with the nitrate anions. The hydrogen bonds are relatively weak, with N···O distances ranging from 3.002 (3) to 3.344 (4) Å. No π–π stacking is apparent in the crystal structure of this compound. It is interesting that the silver(I) ion prefers a trigonal arrangement with the relatively bulky 2,6-diaminopyridine ligand instead of the more commonly preferred linear geometry. The net atomic charge from Mulliken population analysis on the pyridine N atoms is −0.723 for 2,6-diaminopyridine, while it is −0.559 for 4-aminopyridine and −0.515 for pyridine as obtained from *ab initio* calculations at the 6-31G+ level (Kristiansson, 1999). One possible explanation for this observation may be that the higher coordination number with 2,6-diaminopyridine compared with 4-aminopyridine (at similar ligand concentrations) is a result of the increased electrostatic interaction energy. For pyridine complexes obtained from, for example, silver nitrate in pyridine solutions, the composition of the solid solvate appears to be the result of the varying solubility of the salt at different temperatures. Thus, at relatively high temperatures, the formation of the dipyridine complex is favoured, while at low temperatures the existence of the hexasolvate has been suggested on the basis of solubility measurements (Linke, 1958).

Experimental

A mixture of AgNO$_3$ (1 mmol) and either 4-aminopyridine or 2,6-diaminopyridine (6 mmol) in water/ethanol (50:50) was stirred while boiling. The solutions were allowed to evaporate slowly, which afforded X-ray quality crystals. The chosen crystals were coated with a hydrocarbon oil and mounted on a glass fibre.

Compound (I)

Crystal data

[Ag(C$_5$H$_6$N$_2$)$_2$]NO$_3$
M_r = 358.12
Monoclinic, $C2/c$
a = 7.2661 (10) Å
b = 12.2749 (18) Å
c = 14.803 (2) Å
β = 95.084 (2)°
V = 1315.1 (3) Å^3
Z = 4
D_x = 1.809 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1507 reflections
θ = 2.76–27.99°
μ = 1.545 mm^{-1}
T = 295 (2) K
Prism, colourless
0.31 × 0.29 × 0.29 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
3818 measured reflections
1507 independent reflections
1126 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.023
$\theta_{\rm max}$ = 27.99°
$h = -9 \rightarrow 9$
$k = -11 \rightarrow 15$
$l = -18 \rightarrow 18$
Intensity decay: negligible as determined from a repetition of the first 50 frames at the end of the experiment

Refinement

Refinement on F^2
$R[I > 2\sigma(I)]$ = 0.0331
$wR(F^2)$ = 0.0941
S = 0.977
1507 reflections
90 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ < 0.001
$\Delta\rho_{\rm max}$ = 0.60 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.41 e Å^{-3}
Extinction correction: *SHELXTL* (Bruker, 1998)
Extinction coefficient: 9 (6) × 10^{-4}

Table 1
Selected geometric parameters (Å, °) for (I).

Ag1—N1	2.122 (3)	C3—C4	1.390 (5)
N1—C5	1.336 (5)	C3—C2	1.405 (5)
N1—C1	1.342 (5)	C4—C5	1.363 (5)
C3—N2	1.351 (5)	C2—C1	1.359 (5)
N1—Ag1—N1^{i}	174.43 (15)	C4—C3—C2	116.6 (3)
C5—N1—C1	115.5 (3)	C5—C4—C3	119.3 (3)
C5—N1—Ag1	120.6 (2)	C1—C2—C3	119.4 (3)
C1—N1—Ag1	123.8 (2)	N1—C5—C4	124.8 (3)
N2—C3—C4	122.1 (3)	N1—C1—C2	124.4 (3)
N2—C3—C2	121.3 (3)		

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

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$A\cdots$O2^{i}	0.86	2.39	3.189 (5)	154
N2—H2$B\cdots$O1^{ii}	0.86	2.11	2.963 (4)	169

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

Compound (II)

Crystal data

$[Ag(C_5H_7N_3)_3]NO_3$
$M_r = 497.29$
Orthorhombic, $P2_12_12_1$
$a = 8.9276$ (7) Å
$b = 11.1291$ (9) Å
$c = 19.7562$ (15) Å
$V = 1962.9$ (3) Å^3
$Z = 4$
$D_x = 1.683$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 4447 reflections
$\theta = 2.06$–$28.01°$
$\mu = 1.068$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.30 × 0.30 × 0.30 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
11 558 measured reflections
4447 independent reflections
3705 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\rm max} = 28.01°$

$h = -11 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -25 \rightarrow 23$
Intensity decay: negligible as determined from a repetition of the first 50 frames at the end of the experiment

Refinement

Refinement on F^2
$R[I > 2\sigma(I)] = 0.0240$
$wR(F^2) = 0.0545$
$S = 0.937$
4447 reflections
265 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0280P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.93$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.50$ e Å^{-3}
Extinction correction: *SHELXTL* (Bruker, 1998)
Extinction coefficient: 3.5 (3) × 10^{-3}
Absolute structure: Flack (1983)
Flack parameter: 0.017 (19)

Table 3
Selected geometric parameters (Å, °) for (II).

Ag1—N11	2.239 (2)	N1—C1	1.345 (3)
Ag1—N21	2.2601 (18)	N1—C5	1.345 (3)
Ag1—N1	2.4295 (19)	C1—N3	1.386 (3)
N2—C5	1.363 (3)		
N11—Ag1—N21	134.81 (7)	C1—N1—Ag1	113.82 (15)
N11—Ag1—N1	114.35 (7)	C5—N1—Ag1	126.40 (15)
N21—Ag1—N1	109.44 (7)	N1—C5—N2	116.6 (2)
C1—N1—C5	117.8 (2)	N1—C1—N3	115.2 (2)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N2—H2$A\cdots$O2^{i}	0.86	2.15	3.002 (3)	173
N2—H2$B\cdots$O3	0.86	2.29	3.106 (3)	159
N13—H13$A\cdots$N3	0.86	2.36	3.177 (4)	159
N13—H13$B\cdots$O3^{ii}	0.86	2.39	3.199 (3)	156
N12—H12$A\cdots$O2^{i}	0.86	2.39	3.116 (4)	143
N12—H12$A\cdots$O3^{i}	0.86	2.63	3.344 (4)	141
N23—H23$A\cdots$N1	0.86	2.28	3.133 (3)	174
N23—H23$B\cdots$O3^{iii}	0.86	2.37	3.169 (3)	155
N22—H22$B\cdots$O1^{iv}	0.86	2.41	3.213 (4)	155

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

The fraction of Friedel pairs measured for (II) is 0.65.

For both compounds, data collection: *SMART* (Bruker, 1998); cell refinement: *SMART* and *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1082). Services for accessing these data are described at the back of the journal.

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