

Bis(2-aminopyridine- κN^1)(benzoato- κO)silver(I)

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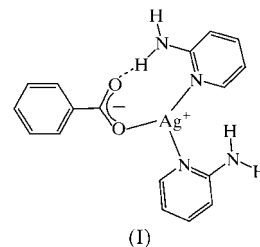
In the title compound, $[\text{Ag}(\text{C}_7\text{H}_5\text{O}_2)(\text{C}_5\text{H}_6\text{N}_2)_2]$, the Ag^{I} atom is tricoordinated by two independent pyridine N atoms and one benzoate O atom in a nearly planar geometry. An intramolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond forms an $S(8)$ graph ring. The packing is built from molecular layers stabilized by two types of $\text{N}-\text{H}\cdots\text{O}$ hydrogen bond. Intermolecular $\text{Ag}\cdots\text{N}$ and intramolecular $\text{Ag}\cdots\text{O}$ contacts were also observed, together with three weak intermolecular $\text{C}-\text{H}\cdots\pi$ interactions.

Comment

Over the past two decades, there has been considerable interest in monovalent coinage-metal compounds because the rich coordination chemistry of these metals can be utilized in the fields of biomimetics, catalysis and materials science (Lehn, 1988). Many polyaza-macrocyclic complexes containing Cu^{II} , Zn^{II} , $\text{Co}^{\text{II,III}}$ and Ni^{II} have been reported. As a heavy metal ion with a d^{10} configuration, Ag^{I} also exhibits rich coordination chemistry. Many factors, such as the natures of the ligands, solvents, anions *etc.*, appear to influence the stereochemistry and stoichiometry of Ag^{I} compounds. All the above factors make it difficult to isolate simple stable monomers or dimers. In previous studies, we obtained and characterized several oligo- Ag^{I} complexes (Zhu *et al.*, 2001; Usman *et al.*, 2003). In this work, we report the crystal structure analysis of bis(2-aminopyridine- κN^1)(benzoato- κO)-silver(I), (I), a new oligo-mononuclear Ag^{I} complex which is stable to light.

The Ag1 atom in (I) is tricoordinated by two pyridine N atoms from two independent 2-aminopyridine ligands and by one O atom from the benzoate ligand (Fig. 1). The $\text{Ag}-\text{N}$ bond lengths [$\text{Ag1}-\text{N1} = 2.230(3)$ Å and $\text{Ag1}-\text{N3} = 2.205(4)$ Å] are within acceptable values and are comparable with those in silver complexes of aminopyridines [*cf.* $2.122(3)$ Å (Kristiansson, 2000), $2.197(4)$ – $2.199(4)$ Å (Li *et*

al., 2002) and $2.283(3)$ – $2.364(6)$ Å (Tong *et al.*, 2002)], whereas the $\text{Ag}-\text{O}$ bond distance [$\text{Ag1}-\text{O1} = 2.344(4)$ Å] is slightly longer than that in terephthalatosilver(I) [$2.175(3)$ Å; Zhu *et al.*, 2003]. The AgN_2O coordination is nearly planar, with atom Ag1 deviating by $0.217(1)$ Å from the O1/N1/N3 plane; the bond angles around Ag1 are listed in Table 1. The planes of the two independent 2-aminopyridine ligands make a dihedral angle of $30.8(3)^\circ$. Within the benzoate moiety, the carboxylate group (C7/O1/O2) is nearly coplanar with the aromatic ring; the dihedral angle between the C6/C7/O1/O2 plane and the plane of the aromatic ring is $4.8(2)^\circ$.



In (I), there is one $S(8)$ graph ring (Etter *et al.*, 1990), *viz.* $\text{O2}-\text{C7}-\text{O1}-\text{Ag1}-\text{N3}-\text{C17}-\text{N4}-\text{H4A}$, maintained by the intramolecular $\text{N4}-\text{H4A}\cdots\text{O2}$ hydrogen bond (see Table 2 for details). This graph ring is not planar and the dihedral angle between the C6/C7/O1/O2 and Ag1/N3/C17/N4 planes is $61.1(1)^\circ$. There is an intramolecular short contact between atoms Ag1 and O2 of $2.863(4)$ Å; this contact is shorter than other $\text{Ag}\cdots\text{O}$ contacts observed in a related structure (average 3.087 Å; Usman *et al.*, 2003).

In the packing, the molecules are interconnected, forming chains parallel to the a direction through intermolecular $\text{N2}-\text{H2B}\cdots\text{O2}^{\text{i}}$ hydrogen bonds [symmetry code: (i) $-x, y + \frac{1}{2}, 1 - z$]. The molecular chains are in turn interconnected through intermolecular $\text{N4}-\text{H4B}\cdots\text{O1}^{\text{ii}}$ hydrogen bonds into

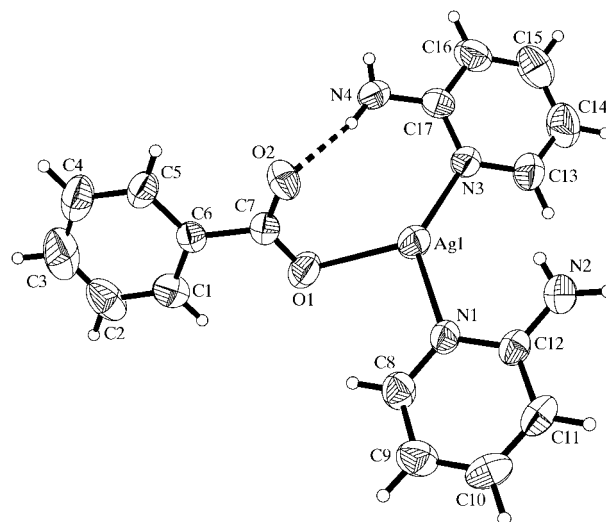


Figure 1
The structure of the title complex, (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. The dashed line denotes the intramolecular $\text{N}-\text{H}\cdots\text{O}$ interaction (Table 2).

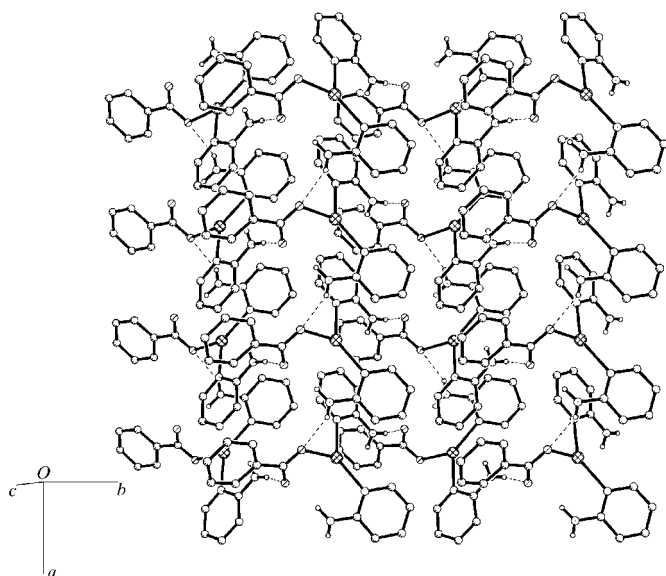


Figure 2
Packing diagram for (I), viewed down the c axis, showing the layers parallel to the ab plane. The dashed lines denote intermolecular N—H...O interactions.

layers [Fig. 2; symmetry code: (ii) $x - 1, y, z$]. The layers stack one above another along the c direction. In this manner, atom O2 facilitates a bifurcated system, and the amino N4—H4 group acts as a multiple hydrogen-bond donor, in contrast to the N2—H2 group, which is a single hydrogen-bond donor. The packing is also stabilized by Ag1...N4($x + 1, y, z$) [3.737 (4) Å] contacts, together with three weak intermolecular C—H... π interactions involving the centroids of the aromatic rings of pyridine C8—C12/N1 ($Cg1$) and benzoate C1—C6 ($Cg3$) (details are given in Table 2).

Experimental

Ag₂O (0.5 mmol, 116 mg) and benzoic acid (1 mmol, 122 mg) were dissolved in ammonium solution (10 ml) and the resulting solution was stirred for *ca* 10 min until a clear solution was obtained. A solution of 2-aminopyridine (2 mmol, 188 mg) in acetonitrile (2 ml) was added to the above solution. The resulting solution was kept in air for 2 d with ammonium gas escaping. Colorless crystals of (I) were collected and washed with water and acetonitrile in turn, and then dried in a vacuum desiccator over CaCl₂ (yield 63%). Analysis calculated for C₁₇H₁₇AgN₄O₂: C 48.94, H 4.11, N 13.43%; found: C 49.05, H 4.18, N 13.29%. IR spectrum (cm⁻¹): 3419 (*w*), 3205 (*m*), 3146 (*m*), 1633 (*m*), 1591 (*s*), 1561 (*s*), 1486 (*s*), 1441 (*s*), 1388 (*vs*), 1323 (*m*), 1271 (*m*), 1156 (*m*), 1004 (*m*), 839 (*m*), 772 (*m*), 722 (*m*), 678 (*m*).

Crystal data

[Ag(C₇H₅O₂)(C₅H₆N₂)₂]
 $M_r = 417.22$
 Monoclinic, $P2_1$
 $a = 6.0261$ (5) Å
 $b = 12.0503$ (10) Å
 $c = 12.3120$ (10) Å
 $\beta = 100.274$ (1)°
 $V = 879.72$ (13) Å³
 $Z = 2$

$D_x = 1.575$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3391 reflections
 $\theta = 2.4$ – 28.3°
 $\mu = 1.16$ mm⁻¹
 $T = 293$ (2) K
 Slab, colorless
 $0.50 \times 0.40 \times 0.38$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.594$, $T_{\max} = 0.667$
 5504 measured reflections
 3019 independent reflections

2671 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\max} = 28.3^\circ$
 $h = -7 \rightarrow 8$
 $k = -15 \rightarrow 10$
 $l = -14 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.087$
 $S = 1.08$
 3019 reflections
 233 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0453P)^2 + 0.1717P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.88$ e Å⁻³
 $\Delta\rho_{\min} = -0.44$ e Å⁻³
 Absolute structure: Flack (1983),
 741 Friedel pairs
 Flack parameter = -0.01 (4)

Table 1

Selected geometric parameters (Å, °).

Ag1—N3	2.205 (4)	O2—C7	1.244 (5)
Ag1—N1	2.230 (3)	N2—C12	1.329 (7)
Ag1—O1	2.344 (4)	N4—C17	1.349 (8)
O1—C7	1.250 (5)		
N3—Ag1—N1	136.4 (2)	N1—Ag1—O1	100.9 (2)
N3—Ag1—O1	119.8 (2)		

Table 2

Hydrogen-bonding geometry (Å, °).

$Cg1$ and $Cg3$ are the centroids of the C8—C12/N1 and C1—C6 rings, respectively

D —H... A	D —H	H... A	D ... A	D —H... A
N2—H2B...O2 ⁱ	0.88 (8)	1.99 (8)	2.851 (6)	163 (7)
N4—H4A...O2	0.90 (7)	2.06 (7)	2.951 (6)	171 (6)
N4—H4B...O1 ⁱⁱ	0.73 (6)	2.22 (6)	2.862 (6)	147 (6)
C10—H10... $Cg3$ ⁱⁱⁱ	0.93	3.17	3.855 (6)	132
C14—H14... $Cg1$ ⁱ	0.93	2.97	3.623 (6)	128
C16—H16... $Cg3$ ^{iv}	0.93	3.11	3.873 (6)	140

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

All H atoms attached to C atoms were fixed geometrically and treated as riding atoms, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, whereas the amino H atoms were located from difference maps and were refined isotropically; the N—H distances are in the range 0.73 (6)–0.90 (7) Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1119). Services for accessing these data are described at the back of the journal.

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