

## Bis( $\mu$ -2-aminopyridine)bis[(trifluoroacetato)silver(I)]

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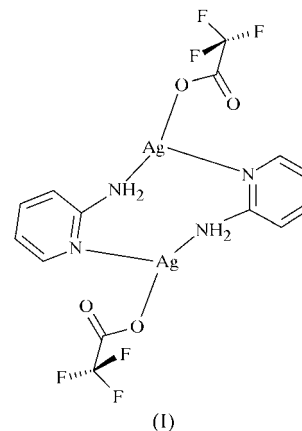
The title compound,  $[\text{Ag}_2(\text{C}_2\text{F}_3\text{O}_2)_2(\text{C}_5\text{H}_6\text{N}_2)_2]$ , is a dinuclear  $\text{Ag}^{\text{I}}$  complex with inversion symmetry. Each Ag atom is three-coordinated by two N atoms from two different 2-aminopyridine ligands and by one O atom from a trifluoroacetate anion, giving an approximately trigonal coordination environment. In the crystal packing, molecules are connected by  $\text{N}-\text{H}\cdots\text{O}$  and  $\text{N}-\text{H}\cdots\text{F}$  hydrogen bonds, forming layers parallel to the (001) plane.

### Comment

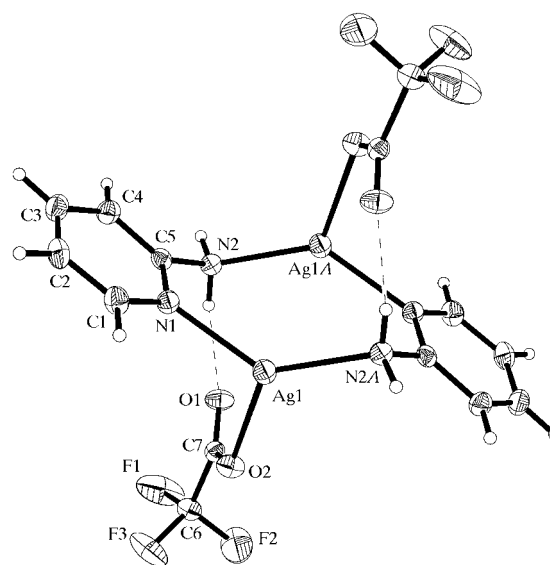
$\text{Ag}^{\text{I}}$  complexes with carboxylate anions as counter-ions or ligands are a group of metal compounds that, because of their wide usage in many fields, have been structurally characterized over the past 30 years (Smith *et al.*, 1996; Kristiansson, 2001; Nomiya *et al.*, 2000; Wei *et al.*, 1998; Zheng *et al.*, 2001). Studying the variety of products in the self-assembly processes between labile metal ions and flexible multidentate ligands is an interesting topic in supramolecular chemistry. The balance between the formation of different structures is often subtle. Factors that affect the coordination topology include not only the highly influential factors of metal and ligand coordination preferences but also anion-based influences. The latter factor is particularly notable in  $\text{Ag}^{\text{I}}$  coordination complexes (Erxleben, 2001; Khlobystov *et al.*, 2001). Owing to the versatile coordination sphere of  $\text{Ag}^{\text{I}}$ , coordination numbers from two to six are possible, and because of the relatively weak nature of many  $\text{Ag}^{\text{I}}$ -ligand interactions, including some anion-Ag interactions, such compounds are particularly susceptible to the influence of weaker supramolecular forces. However, the different nucleophilicities and sizes of the anions must be a significant factor in recognizing the different molecular structures. More work needs to be performed to understand better the controlling effect of anions, which is now becoming an interesting topic in supramolecular chemistry (Cai *et al.*, 2002; Xu *et al.*, 2001).

Recently, we have reported two  $\text{Ag}^{\text{I}}$  complexes with 2-aminopyridine and different counter-anions, *viz.* bis(2-

aminopyridine- $\kappa\text{N}^1$ )(benzoato- $\kappa\text{O}$ )silver(I), (II) (Zhu, Usman *et al.*, 2003) and bis( $\mu$ -4-chlorobenzoato- $\kappa^2\text{O}: \text{O}$ )bis[(2-aminopyridine- $\kappa\text{N}$ )silver(I)], (III) (Zhu *et al.*, 2004). These are both three-coordinate  $\text{Ag}^{\text{I}}$  complexes, although (II) is mononuclear and (III) is O-bridged dinuclear. In order to study the effects of the counter-anions in the construction of  $\text{Ag}^{\text{I}}$  coordination polymers with 2-aminopyridine, the structure of the novel title compound, (I), is reported here.

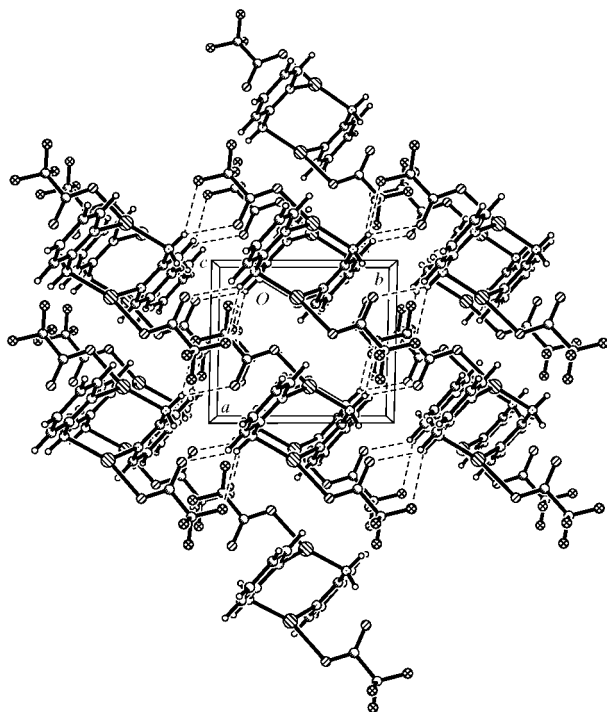


Complex (I) is a dinuclear  $\text{Ag}^{\text{I}}$  complex which exhibits inversion symmetry (Fig. 1). Each  $\text{Ag}^{\text{I}}$  ion in the complex is three-coordinated by two N atoms from two different 2-aminopyridine ligands and by one O atom from a trifluoroacetate anion, giving an approximately trigonal coordination environment (Table 1). Atom Ag1 deviates from the  $\text{N1}/\text{O2}/\text{N2}^i$  trigonal plane by 0.188 (3) Å [symmetry code: (i)  $-x, 1-y, 2-z$ ]. The  $\text{Ag1}-\text{N1}$  bond length [2.269 (3) Å] is slightly longer than the corresponding bond length in (II) [2.230 (3) Å] and is much longer than that in (III) [2.137 (4) Å]. These differences are probably caused by the



**Figure 1**

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Broken lines indicate intramolecular hydrogen bonds. Atoms labeled with the suffix *A* are at the symmetry position  $(-x, 1-y, 2-z)$ .



**Figure 2**  
The crystal packing of (I), viewed along the *c* axis. Broken lines indicate intermolecular hydrogen bonds.

coordination of atom N2 to the other Ag<sup>I</sup> ion in (I), which decreases the electron density around atom N1 and weakens the bond strength between atoms Ag1 and N1. The structure of the present complex, with an eight-membered ring, is very different from that of (II) and (III). In (I), both the amine N atoms and the pyridine N atoms contribute to the coordination of the Ag atoms; however, in (II) and (III), only the pyridine N atoms take part in the coordination, while the amine N atoms participate in the formation of intermolecular N—H···O hydrogen bonds and do not coordinate to the Ag atoms.

The structural differences between (I) and compounds (II) and (III) might be caused by the different counter-ions used in the preparation of the complexes. In (I), the counter-ion is the trifluoroacetate anion, while in (II) and (III), the counter-ions are, respectively, the benzoate and 4-chlorobenzoate anions. The Ag—O(carboxylate) bond in (I) is weakened by the electro-attracting effect of the trifluoromethyl group. In fact, the Ag1—O2 bond length in (I) is slightly longer than the corresponding bond length [2.344 (4) Å] observed in (II) but is much shorter than the Ag···O weak interaction [2.813 (4) Å] observed in another Ag<sup>I</sup>–trifluoroacetate complex, *viz.* bis(4-aminopyridine)silver(I) trifluoroacetate, (IV), which is a mononuclear complex with a linear N(py)—Ag—N(py) bond (Zhu, Zeng *et al.*, 2003). In (I), atom O2 is coordinated to atom Ag1 through a strong chemical bond, while in (IV), the O atom is connected to the Ag atom *via* a weak interaction.

In (I), another eight-membered ring (Ag1/N1/C5/N2/H2C/O1/C7/O2) is formed through an intramolecular N—H···O hydrogen bond. Furthermore, the dinuclear complexes are

linked *via* N—H···O/F hydrogen bonds (Table 2) to form layers parallel to the (001) plane (Fig. 2). There are also  $\pi$ – $\pi$  interactions between the pyridine rings at (*x*, *y*, *z*) and (–*x*, 1 – *y*, 1 – *z*), with a centroid separation of 3.78 (2) Å and a plane-to-plane distance of 3.34 (2) Å.

## Experimental

All reagents and solvents were used as obtained without further purification. Silver trifluoroacetate (0.1 mmol, 22.1 mg) and 2-aminopyridine (0.1 mmol, 9.4 mg) were dissolved in an ammonia solution (10 ml, 30%). The mixture was stirred for about 20 min at room temperature to give a clear colorless solution. The resulting solution was kept in air and, after slow evaporation of the solvent for 10 d, crystals of (I) formed; these were isolated, washed three times with water and dried in a vacuum desiccator using anhydrous CaCl<sub>2</sub> (yield 72%). Elemental analysis, calculated: C 26.7, H 1.9, N 8.9%; found: C 26.5, H 2.0, N 8.9%.

### Crystal data

[Ag <sub>2</sub> (C <sub>2</sub> F <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>6</sub> N <sub>2</sub> ) <sub>2</sub> ]	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 315.01	<i>D<sub>x</sub></i> = 2.286 Mg m <sup>–3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 6.791 (2) Å	Cell parameters from 872 reflections
<i>b</i> = 7.731 (2) Å	$\theta$ = 2.2–23.7°
<i>c</i> = 8.732 (2) Å	$\mu$ = 2.23 mm <sup>–1</sup>
$\alpha$ = 92.01 (3)°	<i>T</i> = 293 (2) K
$\beta$ = 92.17 (3)°	Block, colorless
$\gamma$ = 91.09 (3)°	0.31 × 0.22 × 0.20 mm
<i>V</i> = 457.7 (2) Å <sup>3</sup>	

### Data collection

Bruker SMART CCD area-detector diffractometer	1789 independent reflections
$\omega$ scans	1712 reflections with <i>I</i> > 2σ( <i>I</i> )
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R<sub>int</sub></i> = 0.016
<i>T<sub>min</sub></i> = 0.545, <i>T<sub>max</sub></i> = 0.664	$\theta_{\max}$ = 26.5°
2109 measured reflections	<i>h</i> = –8 → 8
	<i>k</i> = –9 → 9
	<i>l</i> = –10 → 5

### Refinement

Refinement on <i>F</i> <sup>2</sup>	$w = 1/[\sigma^2(F_o^2) + (0.0577P)^2 + 0.418P]$
$R[F^2 > 2\sigma(F^2)] = 0.031$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.084$	( $\Delta/\sigma$ ) <sub>max</sub> < 0.001
<i>S</i> = 1.04	$\Delta\rho_{\max} = 0.81 \text{ e } \text{Å}^{-3}$
1789 reflections	$\Delta\rho_{\min} = -0.87 \text{ e } \text{Å}^{-3}$
137 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.159 (7)

**Table 1**

Selected geometric parameters (Å, °).

Ag1—N1	2.269 (3)	Ag1—O2	2.384 (3)
Ag1—N2 <sup>i</sup>	2.283 (3)	Ag1—Ag1 <sup>i</sup>	3.140 (2)
N1—Ag1—N2 <sup>i</sup>	134.02 (11)	N2 <sup>i</sup> —Ag1—O2	121.71 (10)
N1—Ag1—O2	102.19 (11)		
N1—Ag1—O2—C7	57.9 (3)	N2 <sup>i</sup> —Ag1—O2—C7	–107.8 (3)

Symmetry code: (i) –*x*, 1 – *y*, 2 – *z*.

The diffraction measured fraction  $\theta_{\text{full}}$  was low (0.94) as a result of an unexpected error of the X-ray diffraction instrument during data collection. All H atoms were placed in idealized positions and constrained to ride on their parent atoms, with N—H distances of

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N2-H2A\cdots O1^{ii}$	0.90	2.30	3.095 (4)	146
$N2-H2A\cdots F1^{ii}$	0.90	2.52	3.314 (5)	148
$N2-H2C\cdots O1$	0.90	2.06	2.943 (4)	167

Symmetry code: (ii)  $-x, 2-y, 2-z$ .

0.90 Å and C–H distances of 0.96 Å, and with  $U_{iso}(H)$  values fixed at 0.08 Å<sup>2</sup>.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); 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: OB1201). Services for accessing these data are described at the back of the journal.

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