

## Ammine(2,2'-bipyridine- $\kappa^2N,N'$ )-silver(I) nitrate: a dimer formed by $\pi$ - $\pi$ stacking and ligand-unsupported $Ag \cdots Ag$ interactions

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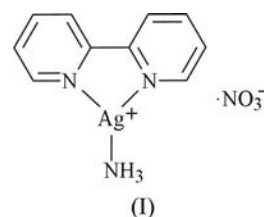
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Reaction of  $AgNO_3$  and 2,2'-bipyridine (bipy) under ultrasonic treatment gave the title compound,  $[Ag(C_{10}H_8N_2)(NH_3)]NO_3$ . The crystal structure consists of dimers formed by two symmetry-related  $Ag^I$ -bipy monomers connected through intra-dimer  $\pi$ - $\pi$  stacking and ligand-unsupported  $Ag \cdots Ag$  interactions. A crystallographic  $C_2$  axis passes through the mid-point of and is perpendicular to the  $Ag \cdots Ag^i(-x + 1, y, -z + \frac{1}{2})$  axis. In addition, each  $Ag^I$  cation is coordinated by one chelating bipy ligand and one ammine ligand, giving a trigonal coordination environment capped by the symmetry-equivalent Ag atom. Molecules are assembled by  $Ag \cdots Ag$ ,  $\pi$ - $\pi$ , hydrogen-bond ( $N-H \cdots O$  and  $C-H \cdots O$ ) and weak  $Ag \cdots \pi$  interactions into a three-dimensional framework. Comparing the products synthesized under different mechanical treatments, we found that reaction conditions have a significant influence on the resulting structures. The luminescence properties of the title compound are also discussed.

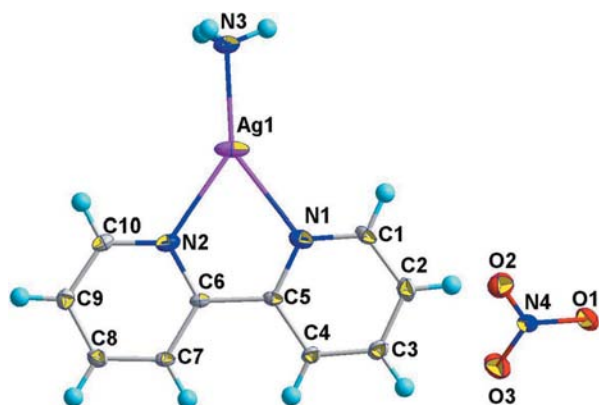
### Comment

Self-assembled coordination structures are one of the most attractive areas of materials research due to their intriguing structural topologies and functional properties such as molecular adsorption, magnetism and luminescence (Biradha *et al.*, 2006; Wu *et al.*, 2009; Blake, Brooks *et al.*, 1999; Blake, Champness *et al.*, 1999; Evans & Lin, 2002; Kitagawa *et al.*, 2004; Yaghi *et al.*, 2003), and much attention has focused on their design and construction. However, the factors that govern the formation of such complexes are complicated and include not only the inherent properties of metal ions and ligand structure, but also anion-directed interactions and reaction conditions (Bu *et al.*, 2003; Kong *et al.*, 2008, 2009). In addition to covalent bonds, noncovalent interactions, such as

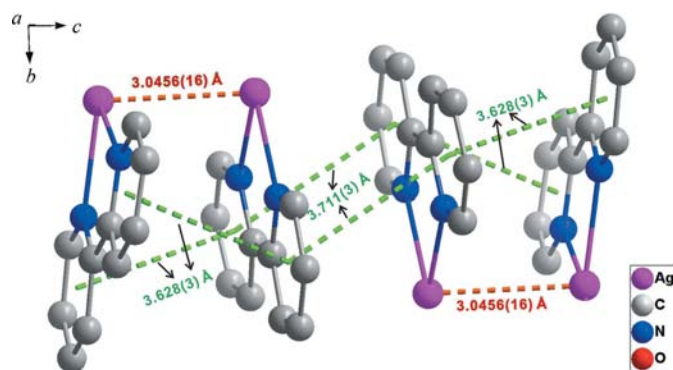
$Ag \cdots Ag$ ,  $\pi$ - $\pi$ , hydrogen-bond and cation- $\cdots\pi$  interactions, also play important roles in controlling molecular packing (Pedireddi *et al.*, 1996; Kolotuchin *et al.*, 1995; Li *et al.*, 2006; Sun *et al.*, 2003; Lough *et al.*, 2000; Massoud & Langer, 2009; Goodgame *et al.*, 2002). Because the central C—C bond of bipyridine (bipy) can rotate freely, bipy cannot just be regarded as a chelating ligand (Kaes *et al.*, 2000; Marchetti *et al.*, 2007), but also as a potential spacer between metal centers by acting as a bridging ligand with an *anti* configuration (Yu *et al.*, 2007; Forniés *et al.*, 1993). Therefore, bipy and its derivatives are widely used in the construction of novel  $Ag^I$ -containing complexes incorporating diverse supramolecular interactions (Hung-Low *et al.*, 2009; Ye *et al.*, 2005). Recently, we have pursued systematic investigations into the assembly of  $Ag^I$  cations 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 *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 complexes or multifunctional coordination polymers. In an attempt to exploit the influence of synthesis conditions on the structures of the  $AgNO_3$ -bipy system, we successfully obtained the title compound, (I), and the known coordination polymer, (II) [*catena*-poly[[2,2'-bipyridine)silver(I)]- $\mu_2$ -nitrate]; Bowmaker *et al.*, 2005], in the same solvent system.



The asymmetric unit of (I) contains one  $Ag^I$  cation, one bipy ligand, one coordinated ammonia molecule and one nitrate anion. As shown in Fig. 1, the  $Ag^I$  cation is coordinated in a trigonal-planar fashion by three N atoms from one bipy ligand and one ammonia molecule, with bond angles ranging from 72.36 (12) to 145.25 (14)°. The  $Ag-N_{bipy}$  bond lengths are identical within experimental error (Table 1) and comparable to reported values (Oxtoby *et al.*, 2002; Fan *et al.*, 2007; Nicola *et al.*, 2007). The pyridyl rings of bipy are nearly coplanar with a twist angle of 4.8 (5)°. With an  $Ag-N$  bond length of 2.135 (4) Å, the coordinated ammonia molecule plays a role as terminator, obstructing aggregation of (I). Because of the labile nature of this  $Ag-N$  bond, the presence of ammonia in the coordination sphere of the metal center offers a potential coordination site in the molecule. Two symmetry-related  $Ag^I$ -bipy monomers aggregate to a dimer with a head-to-head arrangement through intra-dimer  $\pi$ - $\pi$  stacking and a ligand-unsupported  $Ag \cdots Ag$  interaction (Tong *et al.*, 1999), where the  $Ag^I \cdots Ag^I$  interaction [symmetry code: (i)  $-x + 1, y, -z + \frac{1}{2}$ ] has a distance of 3.0456 (16) Å. This is significantly shorter than twice the van der Waals radius of  $Ag^I$  (3.44 Å; Bondi, 1964) and the completed coordination sphere of the Ag centers can thus be described as capped

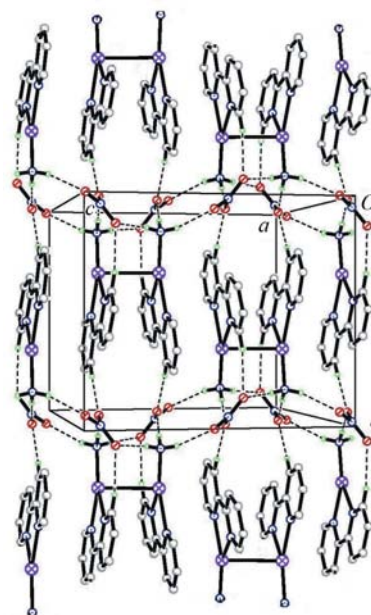

**Figure 1**

The structure of (I), showing the atom-numbering scheme and the coordination environment around the  $\text{Ag}^{\text{I}}$  centre. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius.

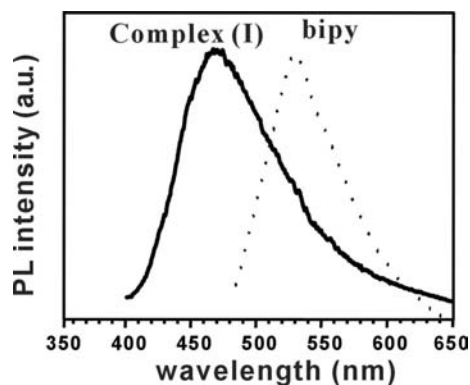

**Figure 2**

A ball-stick perspective view of the  $\pi$ - $\pi$  stacking (green dashed lines in the electronic version of the paper) between the pyridyl rings of neighboring bipy ligands and the  $\text{Ag}\cdots\text{Ag}$  interactions (golden dashed lines). H atoms and nitrate anions have been omitted for clarity.

trigonal planar. The other cases where such short contacts exist between nonbridged  $\text{Ag}^{\text{I}}$  cations are found in  $\text{Ag}(\text{imidazole})_2\text{ClO}_4$  (Eastland *et al.*, 1980) and  $[\text{Cu}(\text{ethylenediamine})_3][\text{Ag}_2(\text{CN})_4]$  (Kappenstein *et al.*, 1988). A crystallographic  $C_2$  axis passes through the mid-point of and is perpendicular to this  $\text{Ag}1\cdots\text{Ag}1^{\text{i}}$  axis. This weak bonding interaction between two  $d^{10}$  cations is possible *via* the participation of  $5s$  and  $5p$  orbitals which are close in energy to the  $4d$  orbitals. Intra-dimer  $\pi$ - $\pi$  stacking also contributes to the reinforcement of this  $\text{Ag}\cdots\text{Ag}$  interaction (Venkatalakshmi *et al.*, 1992). Moreover, the  $\pi$ - $\pi$  stacking [ $Cg1\cdots Cg2^{\text{i}}$  = 3.628(3) Å (intra-dimer) and  $Cg1\cdots Cg2^{\text{vi}}$  = 3.711(3) Å (inter-dimer);  $Cg1$  and  $Cg2$  are the centroids of the N1/C1–C5 and N2/C6–C10 rings, respectively; symmetry codes: (i)  $-x + 1, y, -z + \frac{1}{2}$ ; (vi)  $-x + 1, -y + 1, -z$ ; Fig. 2] and weak  $\text{Ag}\cdots\text{C}$  interactions [ $\text{Ag}1\cdots\text{C}6^{\text{vi}}$  = 3.386(4) Å and  $\text{Ag}1\cdots\text{C}7^{\text{vi}}$  = 3.393(5) Å] act as a 'glue' to reinforce the dimers, forming a column along the  $c$  axis, in which the dimers are arranged in a head-to-tail orientation. In addition, the nitrate anion acts as an acceptor and is hydrogen bonded to


**Figure 3**

A ball-stick perspective view of the three-dimensional supramolecular framework incorporating hydrogen bonds (dashed lines).


**Figure 4**

Photoinduced emission spectrum of (I) (solid line) and free bipy (dotted line) in the solid state.

three different symmetry equivalents of the ammonia molecules (Table 2). Nonclassical  $\text{C}_{\text{pyridyl}}\cdots\text{H}\cdots\text{O}$  hydrogen bonds [average  $\text{C}\cdots\text{O}$  distance = 3.280(5) Å; Table 2] and classical  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds link adjacent columns to form the resulting three-dimensional supramolecular framework (Fig. 3).

The effects of the synthesis conditions on the structure of the  $\text{AgNO}_3$ -bipy system were investigated in the ultrasonic and stirred methods with the same solvent system (methanol-water; 15 ml, 1:2  $v/v$ ). Under stirring, we could only obtain coordination polymer (II), first reported by Bowmaker *et al.* (2005). In the structure of (II), the nitrate anion not only acts as a ligand but also as a bridging anion to link  $\text{Ag}^{\text{I}}$ -bipy cationic units into one-dimensional zigzag chains. The difference between the structures of (I) and (II) originates mainly from the different mechanical treatments which cause the

ammonia molecule and nitrate anion to play different roles in the construction of (I) and (II).

It is known that the free bipy molecule displays a weak luminescence at *circa* 530 nm in the solid state at room temperature. As shown in Fig. 4, compound (I) exhibits an intense emission maximum at 469 nm upon excitation at 345 nm, which may be attributed to the intraligand emission from bipy (Wang *et al.*, 2004). Compared with that of the free bipy molecule, the blue shift and the luminescent enhancement of the emission at 469 nm may be due to the chelation of the bipy ligand to the Ag<sup>I</sup> cation, which effectively increases the rigidity and coplanarity of the ligand and reduces the loss of energy by nonradiative decay of the intraligand emission excited state (Zhang *et al.*, 2003; Qian & Wang, 2002).

## Experimental

All reagents and solvents were used as obtained commercially without further purification. A mixture of AgNO<sub>3</sub> (170 mg, 1 mmol) and 2,2'-bipyridine (156 mg, 1 mmol) was added to a methanol–water solvent mixture (15 ml, 1:2 v/v) under ultrasonic conditions, which helped to dissolve the white precipitate. An aqueous NH<sub>3</sub> solution (25%) was added dropwise to the mixture to give a clear solution. The resulting solution was left to evaporate slowly in the dark at room temperature for several weeks to give crystals of (I) in the form of yellow prisms. The crystals were washed with deionized water and dried in air (yield *ca* 51%, based on Ag). Analysis calculated for C<sub>20</sub>H<sub>22</sub>Ag<sub>2</sub>N<sub>8</sub>O<sub>6</sub>: C 35.01, H 3.23, N 16.33%; found: C 34.95, H 3.14, N 16.27%.

### Crystal data

[Ag(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> )(NH <sub>3</sub> )]NO <sub>3</sub>	$V = 2403 (2) \text{ \AA}^3$
$M_r = 343.10$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 17.685 (9) \text{ \AA}$	$\mu = 1.68 \text{ mm}^{-1}$
$b = 10.690 (5) \text{ \AA}$	$T = 298 \text{ K}$
$c = 12.748 (7) \text{ \AA}$	$0.10 \times 0.08 \times 0.08 \text{ mm}$
$\beta = 94.457 (12)^\circ$	

### Data collection

Oxford Diffraction Gemini S Ultra diffractometer	4406 measured reflections
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2008)	2320 independent reflections
$T_{\min} = 0.850$ , $T_{\max} = 0.877$	2161 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.030$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.112$	
$S = 1.21$	
2320 reflections	$\Delta\rho_{\text{max}} = 0.85 \text{ e \AA}^{-3}$
172 parameters	$\Delta\rho_{\text{min}} = -0.59 \text{ e \AA}^{-3}$
6 restraints	

The aromatic H atoms were generated geometrically (C–H = 0.93 Å) and allowed to ride on their parent atoms in the riding-model approximation, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The positions of the ammonia H atoms were located from difference maps and refined with the N–H distances restrained to 0.89 (2) Å, the H···H distances restrained to be similar with a tolerance s.u. of 0.04 Å and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N})$ .

**Table 1**

Selected geometric parameters (Å, °).

Ag1–N3	2.135 (4)	Ag1–N1	2.302 (3)
Ag1–N2	2.296 (3)	Ag1–Ag1 <sup>i</sup>	3.0456 (16)
N3–Ag1–N2	142.34 (14)	N3–Ag1–Ag1 <sup>i</sup>	93.86 (11)
N3–Ag1–N1	145.25 (14)	N2–Ag1–Ag1 <sup>i</sup>	100.92 (8)
N2–Ag1–N1	72.36 (12)	N1–Ag1–Ag1 <sup>i</sup>	75.91 (8)

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

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3–H3A···O1 <sup>ii</sup>	0.87 (2)	2.14 (2)	2.998 (6)	170 (5)
N3–H3B···O3 <sup>iii</sup>	0.89 (2)	2.23 (2)	3.110 (5)	169 (4)
N3–H3C···O2 <sup>iv</sup>	0.88 (2)	2.30 (2)	3.177 (5)	172 (5)
C1–H1···O3 <sup>ii</sup>	0.93	2.39	3.307 (5)	169
C7–H7···O1 <sup>v</sup>	0.93	2.27	3.192 (5)	169
C10–H10···O2 <sup>i</sup>	0.93	2.58	3.340 (6)	139

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg, 2008) and *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* and *publCIF* (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3026). Services for accessing these data are described at the back of the journal.

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