

Bis(di-2-pyridylamine- κ^2N^2,N^2')-silver(I) trifluoromethanesulfonate: polar arrangement of trifluoromethanesulfonate anions in a pseudo-centrosymmetric framework of coordination cations

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Received 6 October 2010

Accepted 28 October 2010

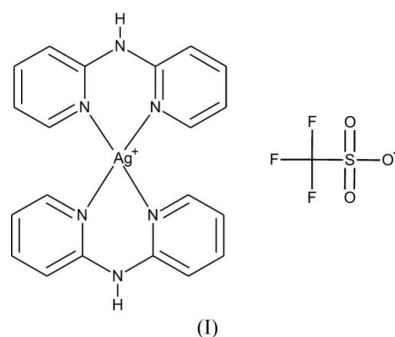
Online 30 October 2010

The asymmetric unit of the title compound, $[\text{Ag}(\text{C}_{10}\text{H}_9\text{N}_2)_2]\text{CF}_3\text{SO}_3$ or $[\text{Ag}(\text{dpa})_2]\text{OTf}$ (dpa is di-2-pyridylamine and OTf is the trifluoromethanesulfonate anion), contains two $[\text{Ag}(\text{dpa})_2]^+$ coordination cations and two OTf anions. The coordination geometry of the Ag^{I} atom is intermediate between square-planar and tetrahedral, with similar deformations at the two symmetry-independent metal centres. The dpa ligands coordinate in a bidentate chelating mode. The OTf anions are in the outer coordination sphere and bridge the coordination cations *via* $\text{N}-\text{H}\cdots\text{O}$ interactions to form two symmetry-independent hydrogen-bonded chains. The $[\text{Ag}(\text{dpa})_2]^+$ cations are arranged *via* interactions involving the aromatic groups into a pseudo-centrosymmetric three-dimensional framework with two types of channels, each confining congeners of one of the symmetry-independent anions. The most interesting feature of this structure is its bulk polarity resulting from an approximately parallel alignment of the anions in the channels.

Comment

The interest of coordination and supramolecular chemists in Ag^{I} is mainly related to the coordination flexibility of this d^{10} ion and its tendency to form strong complexes with nitrogen-donor ligands. It has been shown that di-2-pyridylamine (dpa) can coordinate to Ag^{I} both in its deprotonated and neutral forms. In the former case, a charge-neutral one-dimensional coordination polymer is formed with all three N-atom donors involved in the coordination to Ag centres (Liao *et al.*, 2001). In turn, neutral dpa can act as a bidentate ligand, in chelating or bridging mode, with a secondary amine group available as a donor for hydrogen bonding. It has been shown by Burgos *et al.* (2003) that in the reaction of silver(I) trifluoromethanesulfonate, $[\text{Ag}(\text{OTf})]$, with neutral dpa, depending on the

synthetic conditions employed, a discrete molecular complex $[\text{Ag}(\text{dpa})_2]\text{OTf}$, (I), and a coordination polymer $[\text{Ag}(\text{OTf})(\text{dpa})]_n$, (II), can be formed. No crystal data were reported in the original paper, but the structure of (II) was published later on (Jones *et al.*, 2006), revealing a one-dimensional polymeric structure with a bridging dpa ligand and a four-coordinate silver centre. An interesting feature of this structure was that one of the coordination bonds was formed to a pyridine C atom. Recently, in the course of our work on silver complexes with N-donor ligands, the synthesis of (I) was repeated using acetonitrile as solvent, and good-quality single crystals were obtained. In this paper, we report the crystal structure of (I), where the coordination cations form a virtually centrosymmetric pattern; however, the OTf anions show polar packing, resulting in an overall noncentrosymmetric structure.



The asymmetric unit of (I) consists of two $[\text{Ag}(\text{dpa})_2]^+$ coordination cations and two OTf anions (Fig. 1). In accord with spectroscopic studies (Burgos *et al.*, 2003), the dpa units act as bidentate chelating ligands, coordinating to Ag through both pyridyl N atoms to form six-membered rings. The coordination geometry at Ag1 and Ag2 is intermediate between square-planar and tetrahedral, with similar deformations at the two metal centres (Table 1). The dpa ligands form one shorter and one longer Ag—N bond, with the former ranging

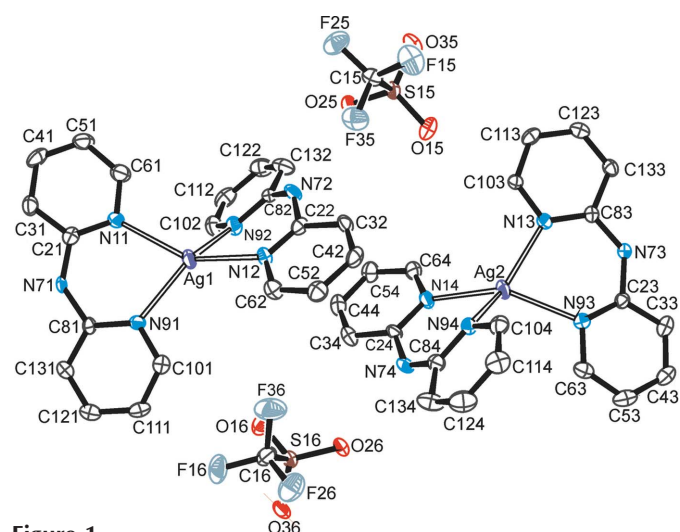
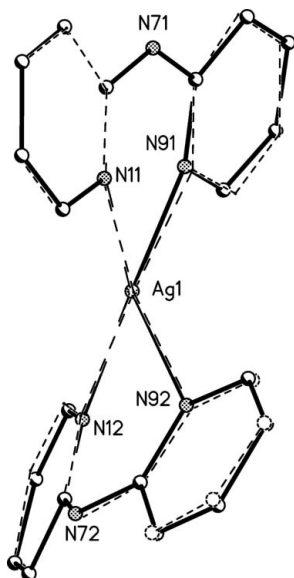


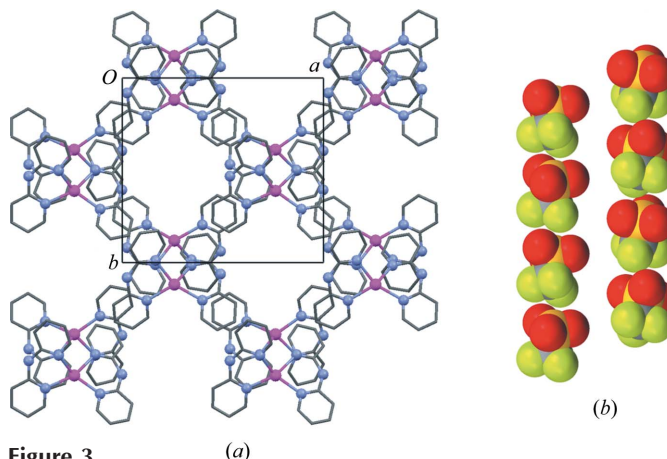
Figure 1
The asymmetric unit of (I), with displacement ellipsoids shown at the 50% probability level. H atoms have been omitted for clarity.


Figure 2

Superposition of the two symmetry-independent coordination cations. The coordination cation with Ag1 is shown with larger spheres and full lines. All atoms, excluding H atoms, were fitted; the r.m.s. deviation of the fitted atoms is 0.097 Å.

from 2.269 (3) to 2.305 (3) Å [mean 2.283 (16) Å] and the longer bonds in the range 2.337 (3)–2.373 (3) Å [mean 2.357 (15) Å]. The structure of the two coordination cations is similar, as shown by their superposition in Fig. 2. They interact *via* two types of contacts involving the aromatic groups: (a) offset π – π stacking interactions between the N12/C62 and N14/C64 pyridine rings of the two symmetry-independent cations [with a centroid–centroid distance of 3.662 (7) Å, a dihedral angle between the best planes of 1.72 (13)°, and a distance between the N12–C62 ring centroid and the plane of the N14–C64 ring of 3.389 (1) Å]; (b) through edge-to-face contacts (C–H $\cdots\pi$ and C–H \cdots C) between the pyridine rings belonging to the cations of the same type (Table 2). These interactions assemble the [Ag(dpa)₂]⁺ units into a virtually centrosymmetric three-dimensional framework, not deviating much from *P*2₁/*c* symmetry, with the pseudo-inversion centre at ($\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{2}$) relating the two symmetry-independent [Ag(dpa)₂]⁺ units (Fig. 3a).

There are two symmetry-independent channels formed in the cationic framework that extend along the *c* axis and are related by a pseudo-inversion centre. These channels, confining OTf anions, have their long axes situated on glide planes at *y* = (0, $\frac{1}{2}$). One can see from Fig. 3(b), showing the arrangement of the anions in the two channels, that all polar OTf anions have their C–S axes oriented in nearly the same direction, *viz.* in the crystal studied, in the positive direction of the *c* axis, and that this packing of the anions renders the crystal structure noncentrosymmetric. This is an unusual behaviour for the OTf anion, which generally does not induce bulk polarity in the absence of chiral molecules. The OTf anions confined in the channels bridge the coordination cations *via* two N–H \cdots O hydrogen bonds involving the N–H groups of dpa ligands from two cations. Two symmetry-


Figure 3

(a) The pseudo-centrosymmetric three-dimensional framework of the coordination cations with anions removed from the channels, viewed along the *c* axis, and (b) the polar arrangement of the anions in the two symmetry-independent channels, viewed along the *b* axis, with [001] vertical.

independent hydrogen-bonded chains are extended in the [201] direction which is inclined to the *c* axis by 72.5°.

Experimental

AgOTf and dpa were purchased from Aldrich and used as received. AgOTf (0.030 g, 0.117 mmol) was added to an acetonitrile solution (5 ml) of dpa (0.040 g, 0.234 mmol). The solution was stirred for 10 min and left for slow evaporation. Colourless needle-shaped crystals formed within 2 weeks.

Crystal data

[Ag(C ₁₀ H ₉ N ₂) ₂]CF ₃ SO ₃	<i>V</i> = 2270.70 (10) Å ³
<i>M_r</i> = 599.34	<i>Z</i> = 4
Monoclinic, <i>Pc</i>	Mo <i>K</i> α radiation
<i>a</i> = 15.1215 (4) Å	μ = 1.04 mm ^{−1}
<i>b</i> = 13.2206 (3) Å	<i>T</i> = 130 K
<i>c</i> = 11.9113 (3) Å	0.30 × 0.10 × 0.10 mm
β = 107.527 (3)°	

Data collection

Kuma KM-4 CCD (κ geometry) diffractometer	18407 measured reflections
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007)	8833 independent reflections
<i>T</i> _{min} = 0.735, <i>T</i> _{max} = 0.913	7362 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.021

Table 1

Selected geometric parameters (Å, °).

Ag1–N91	2.284 (3)	Ag2–N14	2.269 (3)
Ag1–N12	2.305 (3)	Ag2–N93	2.273 (3)
Ag1–N92	2.357 (3)	Ag2–N13	2.337 (3)
Ag1–N11	2.373 (3)	Ag2–N94	2.361 (3)
N91–Ag1–N12	120.66 (8)	N14–Ag2–N93	120.92 (10)
N91–Ag1–N92	139.76 (10)	N14–Ag2–N13	146.92 (10)
N12–Ag1–N92	80.44 (9)	N93–Ag2–N13	81.55 (10)
N91–Ag1–N11	81.47 (10)	N14–Ag2–N94	80.54 (10)
N12–Ag1–N11	148.62 (10)	N93–Ag2–N94	136.16 (10)
N92–Ag1–N11	96.61 (10)	N13–Ag2–N94	100.03 (9)

Table 2

Hydrogen-bond geometry (Å, °).

 C_{g1} , C_{g2} and C_{g3} are the centroids of the N12-, N91- and N13-containing pyridine rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N72—H72···O25	0.90	2.08	2.912 (4)	154
N74—H74···O26	0.90	1.95	2.842 (3)	171
N71—H71···O35 ⁱ	0.90	2.08	2.976 (3)	179
N73—H73···O36 ⁱⁱ	0.90	2.06	2.939 (4)	164
C122—H122··· C_{g1} ⁱⁱⁱ	0.95	2.95	3.622 (6)	129
C41—H41··· C_{g2} ^{iv}	0.95	2.76	3.561 (6)	143
C43—H43··· C_{g3} ^v	0.95	2.82	3.603 (6)	140
C124—H124···C64 ^{vi}	0.95	2.87	3.373 (6)	114

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

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.054$

$S = 1.03$

8833 reflections

631 parameters

2 restraints

H-atom parameters constrained

$\Delta\rho_{\max} = 0.57 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\min} = -0.64 \text{ e } \text{Å}^{-3}$

Absolute structure: Flack (1983),

3456 Friedel pairs

Flack parameter: 0.009 (12)

The absolute structure of (I) was determined from anomalous dispersion effects. H atoms of the N—H groups were located in difference electron-density maps and N—H bond lengths were standardized to 0.90 Å. $U_{\text{iso}}(\text{H})$ values were constrained to $1.2U_{\text{eq}}(\text{N})$.

All other H atoms were initially identified in difference maps but were placed at calculated positions, with C—H = 0.95 Å, and were refined as riding on their carrier atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3242). Services for accessing these data are described at the back of the journal.

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