

catena-Poly[[trifluoromethanesulfonato- κ O]silver(I)]- μ -di-2-pyridylamine- κ^2 N²:N^{2'}], a chain polymer with short Ag \cdots C contacts

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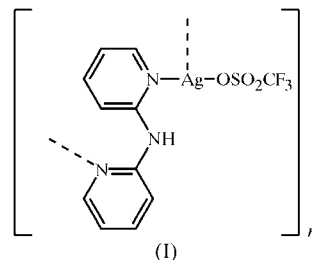
The title compound, [Ag(CF₃O₃S)(C₁₀H₉N₃)]_n, is a chain polymer in which neighbouring monomeric units are related by a glide plane. The silver centre is four-coordinate; the donor atoms are one trifluoromethanesulfonate O atom and one pyridine N atom from each of two symmetry-related dipyridylamines, and an additional and unexpected Ag \cdots C contact [2.6464 (16) Å] is observed to a pyridine C atom. The chains are reinforced by one classical N—H \cdots O and two ‘weak’ C—H \cdots O hydrogen bonds.

Comment

We are interested in complexes of the ligand di-2-pyridylamine (DPA), and have reported some of its complexes with silver, gold and palladium, together with the structure of [Ag(DPA)(PPh₃)](OTf) (OTf is trifluoromethanesulfonate; Burgos *et al.*, 2003). This displays, to a first approximation, three-coordinate silver, the donor atoms being the P atom (of PPh₃) and both pyridine N atoms of the same DPA ligand. An additional Ag \cdots O interaction of 2.725 (3) Å, supported by an N—H \cdots O hydrogen bond, links the molecules to form chains. The synthesis of the title compound, [Ag(OTf)(DPA)]_n, (I), was reported at the time, but not the structure, which we present here.

The asymmetric unit of (I) is presented in Fig. 1. It is striking that the compound does not display coordination through the pyridine N atoms and a trifluoromethanesulfonate O atom, as might perhaps have been expected. Instead, coordination occurs *via* one pyridine N atom (N11), trifluoromethanesulfonate atom O3 and a second pyridine N atom (N21) of a different asymmetric unit (the latter is not shown in Fig. 1; the extended structure is discussed below). The Ag—N distances (Table 1) are broadly similar to those of [Ag(DPA)(PPh₃)](OTf) [Ag—N = 2.264 (2) and 2.283 (2) Å],

but the Ag—O distance is appreciably shorter and may be assumed to correspond to a stronger bonding interaction.



Within the asymmetric unit there is also an unexpected contact from silver to a ring C atom, namely Ag \cdots C23, approximately perpendicular to the ring (the angle between the vector Ag \cdots C23 and the mean ring plane is 70.7°). In contrast to the more familiar situation, for example, in the complex of silver perchlorate and benzene [Ag—C = 2.565 (1) Å in a low-temperature neutron study (McMullan *et al.*, 1997)], the Ag atom is coordinated to just this one C atom rather than at equal distances to two neighbouring ring C atoms; the distances to atoms C22 and C24 are much greater at 3.049 (2) and 3.260 (2) Å, respectively. There are difficulties involved in searching the Cambridge Structural Database (Version 5.27; Allen, 2002) for such contacts (are they coded as bonds or not?), but we were unable to find a further example of such a short contact involving a pyridine ligand.

The dimensions of the DPA ligand may be regarded as normal, although the N11—C12 bond is somewhat short at 1.337 (2) Å. The interplanar angle between the rings is 34.60 (5)°. More informative are the torsion angles N11—C12—N1—C22 and N21—C22—N1—C12 (Table 1), which are very approximately syn- and antiperiplanar, respectively. The additional contact to the Ag atom results in no significant changes to the dimensions of the N21/C22—C26 ring.

The extended structure most importantly involves an Ag—N21 bond to a neighbouring molecule generated by the *n*-glide plane. This leads to four-coordination at the Ag atom and to the formation of a chain polymer parallel to the *y* axis (Fig. 2). Within this polymer, one classical N—H \cdots O hydrogen bond and two ‘weak’ C—H \cdots O interactions (Desiraju & Steiner, 1999) (the first three hydrogen bonds of Table 2), including a bifurcated system involving the common acceptor O2, presumably act as stabilizing features; a long Ag \cdots O1 contact

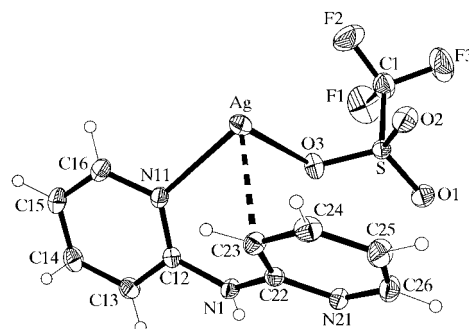


Figure 1
The asymmetric unit of the title compound. Displacement ellipsoids represent 50% probability levels.

within the chain [3.2079 (14) Å] is probably less relevant and is not included in the figure. There are short C—H...X (X = O and F) contacts (Table 2) between neighbouring chains.

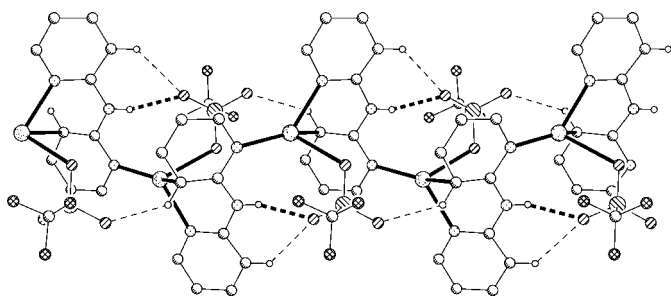


Figure 2
The packing of the title compound, viewed perpendicular to the xy plane. Secondary interactions are indicated by dashed lines (thick, N—H...O bonds; thin, C—H...O bonds). The origin is at the lower right-hand corner, with the x and y axes vertical and horizontal, respectively.

Experimental

The title complex was synthesized as described by Burgos *et al.* (2003) and recrystallized from dichloromethane/pentane.

Crystal data

[Ag(CF ₃ O ₃ S)(C ₁₀ H ₉ N ₃)]	$Z = 4$
$M_r = 428.14$	$D_x = 2.060 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 10.9077 (8) \text{ \AA}$	$\mu = 1.66 \text{ mm}^{-1}$
$b = 9.9610 (6) \text{ \AA}$	$T = 143 (2) \text{ K}$
$c = 13.2994 (8) \text{ \AA}$	Tablet, colourless
$\beta = 107.223 (3)^\circ$	$0.21 \times 0.10 \times 0.04 \text{ mm}$
$V = 1380.21 (16) \text{ \AA}^3$	

Data collection

Bruker SMART 1000 CCD diffractometer	22658 measured reflections
ω and φ scans	4029 independent reflections
Absorption correction: multi-scan (SADABS; Bruker, 1998)	3394 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.803$, $T_{\max} = 0.936$	$R_{\text{int}} = 0.050$
	$\theta_{\text{max}} = 30.0^\circ$

Table 1

Selected geometric parameters (Å, °).

Ag—N21 ⁱ	2.2072 (14)	Ag...C23	2.6464 (16)
Ag—N11	2.2817 (13)	N1—C22	1.384 (2)
Ag—O3	2.5484 (13)	N1—C12	1.387 (2)
N21 ⁱ —Ag—N11	133.59 (5)	N11—Ag—C23	71.80 (5)
N21 ⁱ —Ag—O3	114.14 (5)	O3—Ag—C23	92.46 (5)
N11—Ag—O3	91.06 (4)	C22—N1—C12	127.31 (14)
N21 ⁱ —Ag—C23	139.34 (5)		
C22—N1—C12—N11	20.0 (2)	C12—N1—C22—N21	−159.64 (15)

Symmetry code: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.058$
 $S = 0.99$
 4029 reflections
 203 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0348P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.71 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C23—H23...O1 ⁱ	0.95	2.46	3.213 (2)	136
N1—H1...O2 ⁱⁱ	0.790 (15)	2.109 (16)	2.8739 (19)	163.2 (18)
C13—H13...O2 ⁱⁱ	0.95	2.53	3.278 (2)	136
C25—H25...O3 ⁱⁱⁱ	0.95	2.48	3.275 (2)	142
C14—H14...O1 ^{iv}	0.95	2.63	3.462 (2)	147
C15—H15...F3 ^{iv}	0.95	2.63	3.372 (2)	135
C16—H16...F2 ^v	0.95	2.60	3.397 (2)	142

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

The amine H atom was refined freely but with an N—H bond-length restraint of 0.84 (2) Å. Other H atoms were included using a riding model, with fixed C—H bond lengths of 0.95 Å; $U_{\text{iso}}(\text{H})$ values were fixed at $1.2U_{\text{eq}}$ of the parent atom.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XP (Siemens, 1994); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3040). Services for accessing these data are described at the back of the journal.

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