Synthesis, crystal structure and photophysical properties of bis[2,6-difluoro-3-(pyridin-2-yl)pyridine-κN](trifluoromethanesulfonato-κO)silver(I)

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In the title compound, [Ag(CF₃SO₃)(C₁₀H₆F₂N₂)₂], the Ag⁺ centre adopts a highly distorted trigonal–planar coordination environment resulting from its coordination by one O atom of the trifluoromethanesulfonate anion and the pyridine N atoms of two crystallographically independent 2',6'-difluoro-2,3'-bipyridine ligands, which display very similar conformations to one another. Pairwise Ag⋯O–SO₂CF₃ [Ag⋯O = 2.8314 (14) Å] interactions and intermolecular C–H⋯O interactions between inversion-related units lead to the formation of an eight-membered cyclic dimer in which the silver atoms are separated by 6.2152 (3) Å. In the crystal, the dimers are linked through C–H⋯O hydrogen bonds, halogen⋯π and weak π⋯π stacking interactions, resulting in the formation of a three-dimensional supramolecular network. The title compound exhibits a strong and broad emission band from 400 nm to 550 nm in solution and its photoluminescence quantum efficiency is estimated to be ca 0.2, indicating that the title compound could have applications as an emitting material in organic light-emitting diodes (OLEDs).

1. Chemical context

Recently, great attention has been paid to 2,3'-bipyridine-based IrIII and PtII complexes by many researchers because of their applicability to OLEDs and solid-state lighting (Kang et al., 2021; Reddy & Bejoymohandas, 2016). In particular, 2',6'-difluoro-2,3'-bipyridine complexes of iridium(III) are considered to be strong candidates as both blue triplet emitters in phosphorescent organic light-emitting diodes (PHOLEDs) and single dopants in white organic light-emitting diodes (WOLEDs) (Zaen et al., 2019; Kang et al., 2020; Lee et al., 2018). Despite these investigations, reports regarding the structures and photoluminescence properties of 2,3'-bipyridine-based group-11 metal complexes are scarce, and related research is limited (Li et al., 2019). Among the group-11 elements, coordination polymers of Ag⁺ have been demonstrated to exhibit structural diversity as a result of the d10 configuration of the metal ion (Lee et al., 2020). Moreover, the various coordination environments around the Ag⁺ centre are generally constructed by the ligands, solvent molecules, and counter-anions (Lee et al., 2016). Until now, there has been no report with respect to an Ag⁺ complex bearing a 2',6'-difluoro-2,3'-bipyridine ligand as compared to 2,2'-bipyridine-based Ag⁺ complexes (Pal et al., 2020). This fact prompted us to investigate the structures and luminescent properties of
2,3′-bipyridine-based Ag⁺ complexes: in this study, we report the preparation, structural characterization and luminescent properties of an Ag⁺ complex of 2,6′-difluoro-2,3′-bipyridine.

2. Structural commentary

The asymmetric unit in the title compound consists of an Ag⁺ cation, a CF₃SO₃⁻ trifluoromethanesulfonate anion and two crystallographically independent C₁₀H₆F₂N₂ 2,6′-difluoro-2,3′-bipyridine ligands, which adopt very similar conformations, such that the dihedral angles between the pyridyl rings in the N1- and N3-containing molecules are 53.11 (5) and 53.10 (7)°, respectively. As shown in Fig. 1, the Ag⁺ ion is coordinated by two pyridine N atoms (N2 and N4) from two 2,6′-difluoro-2,3′-bipyridine ligands and one O atom from the trifluoromethanesulfonate anion, forming a highly distorted trigonal–planar geometry. Selected bond lengths and angles around the Ag¹ atom are given in Table 1: the N—Ag—N and N—Ag—O angles fall in the range 86.55 (5)—148.65 (5)°, deviating significantly from an ideal trigonal–planar geometry. This may reflect the influence of an additional Ag···O—SO₂CF₃ interaction between the metal ion and an O atom of an adjacent trifluoromethanesulfonate anion [Ag¹···O₂⁻ = 2.8314 (14) Å; black dashed lines in Fig. 2; symmetry code: (i) −x + 1, −y, −z + 1]. The Ag⁺ atom is displaced out of the trigonal N₂, N₄, O₁ coordination plane by 0.1057 (9) Å. The C₆—C₁₀/N₂ and C₁₆—C₂₀/N₄ pyridine rings coordinated to the Ag⁺ centre are tilted by 25.75 (10)° with respect to each other. The pairwise Ag···O links lead to the formation of an eight-membered [Ag—O—S—O—]₂ cyclic dimer, in which the silver atoms are separated by 6.2152 (3) Å. The cyclic dimer is consolidated by C—H···O interactions (Table 2; yellow dashed lines in Fig. 2).

3. Supramolecular features

In the extended structure, the dimers are linked through C₁₉—H₁₉···O₃ hydrogen bonds (Table 2) and weak π···π stacking interactions [yellow and sky-blue dashed lines in...
The two-dimensional supramolecular network formed through C—H···O hydrogen bonds (yellow dashed lines), F···π (red dashed lines) and π···π stacking (sky-blue dashed lines) interactions. For clarity, H atoms not involved in the intermolecular interactions have been omitted. Atom colours as in Fig. 2.

The three-dimensional supramolecular network formed through F···π (red dashed lines) and π···π stacking (sky-blue dashed lines) interactions. For clarity, H atoms not involved in the intermolecular interactions have been omitted. Atom colours as in Fig. 2.

The two-dimensional supramolecular network formed through C—H···O hydrogen bonds (yellow dashed lines), F···π (red dashed lines) and π···π stacking (sky-blue dashed lines) interactions. For clarity, H atoms not involved in the intermolecular interactions have been omitted. Atom colours as in Fig. 2.

The three-dimensional supramolecular network formed through F···π (red dashed lines) and π···π stacking (sky-blue dashed lines) interactions. For clarity, H atoms not involved in the intermolecular interactions have been omitted. Atom colours as in Fig. 2.

Figure 3
The two-dimensional supramolecular network formed through C—H···O hydrogen bonds (yellow dashed lines), F···π (red dashed lines) and π···π stacking (sky-blue dashed lines) interactions. For clarity, H atoms not involved in the intermolecular interactions have been omitted. Atom colours as in Fig. 2.

The three-dimensional supramolecular network formed through F···π (red dashed lines) and π···π stacking (sky-blue dashed lines) interactions. For clarity, H atoms not involved in the intermolecular interactions have been omitted. Atom colours as in Fig. 2.

Table 2
Hydrogen-bond geometry (Å, †).

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|----------|
| C10—H10···O2i | 0.95 | 2.60  | 3.239 (2) | 125 |
| C13—H13···O2i | 0.95 | 2.63 | 3.173 (2) | 119 |
| C13—H13···O3ii | 0.95 | 2.50 | 3.400 (2) | 159 |
| C19—H19···O3ii | 0.95 | 2.53 | 3.294 (2) | 137 |
| C20—H20···O1 | 0.95 | 2.55 | 3.197 (2) | 126 |

Symmetry codes: (i) −x + 1, −y, −z + 1; (ii) x, y, z; (iii) x + 1, y, z; (iv) −x + 1, −y, −z.

3.1424 (19) Å; Cg1···Cg1iv = 4.2435 (13) Å; Cg1 and Cg2 are the centroids of the C1–C5/N1 and C6–C10/N2 rings, respectively; symmetry code: (iv) −x + 1, −y, −z, resulting in the formation of a three-dimensional supramolecular network.

4. Luminescent properties

In CH2Cl2 solution, the title compound exhibits a strong and broad emission band with λmax = 400 nm, as shown in Fig. 5. This emission band may arise from π···π* transitions of the bipyridine ligand because the absorption of the title compound is very similar to that of the free ligand. Interestingly, upon the complexation of ligand with the Ag(CF3SO3) unit, significant blue-shifted emissions (> 50 nm) are observed as compared with bipyridine based IrIII complexes (Lee et al., 2009). Moreover, a broad emission from 400 nm to 500 nm in the title compound may be due to the predominantly fluorescent emission from the 2,0,6,0-difluoro-2,3-bipyridine ligand because the emission maximum of the free ligand, i.e., phosphorescent emission, occurs at approximately 450 nm (triplet energy, T1 = 2.82 eV). The observed emission of the title compound is therefore attributed to ligand-centered π···π* transitions with a minor contribution of an Ag-based metal-to-ligand charge-transfer transition. Similar dual-emission behaviour has been noted for some AgI complexes with 2-methylthiothiazole (Rogovoy et al., 2019).
Table 3
Experimental details.

| Crystal data | Chemical formula [Ag(CF₃O₃S)(C₁₀H₆F₂N₂)₂] |
|--------------|-----------------------------------------|
| Mₑ          | 641.28                                  |
| Temperature (K) | 193                                    |
| a, b, c (Å) | 9.0627 (2), 10.9637 (3), 12.5727 (3)    |
| α, β, γ (°) | 82.4508 (11), 73.7215 (11), 71.5490 (11) |
| V (Å³)      | 1136.26 (5)                             |
| Z            | 2                                       |
| Radiatn type | Mo Ka                                   |
| μ (mm⁻¹)    | 1.07                                    |
| Crystal size (mm) | 0.38 × 0.33 × 0.32                      |

| Data collection | Diffractometer | Absorption correction |
|-----------------|----------------|-----------------------|
|                 | Bruker APEXII CCD | Multi-scan (SADABS, Bruker, 2014) |

| Refinement | R[F² > 2σ(F²)], wR(F²), S | No. of reflections | No. of parameters | H-atom treatment | Δρ_max, Δρ_min (e Å⁻³) |
|------------|---------------------------|--------------------|-------------------|------------------|-----------------------|
|            | 0.025, 0.067, 1.12        | 5623               | 334               | H-atom parameters constrained | 0.33, −0.76          |

Computer programs: APEX2 and SAINT (Bruker, 2014), SHELXS97 and SHELXTL (Sheldrick, 2008), SHELXL2014/7 (Sheldrick, 2015), DIAMOND (Brandenburg, 2010) and pubCIF (Westrip, 2010).

and pyridylphosphine ligands (Baranov et al., 2019). The emission intensity of the title compound was also higher than that of free ligand, as shown in Fig. 5. The photoluminescence quantum efficiency of the title compound was estimated to be ca 0.2 (Fig. 5, inset). Such an efficiency is large enough to potentially use the title compound as the emitting material in an organic light-emitting diode (OLED) application.

5. Database survey
A survey of SciFinder (SciFinder, 2021) for transition-metal complexes bearing the 2,6-difluoro-2,3′-bipyridine moiety as a ligand gave 25 hits. They include reports about the crystal structures and photophysical properties of IrIII and PtIV complexes based on this ligand (HOVHAC, Lee et al., 2009; OHUMUB01, Lee et al., 2015; JUDZAL, Park et al., 2015). The survey revealed no exact matches for the reported structure of the title complex. To the best of our knowledge, this is the first crystal structure reported for a silver complex with the title ligand.

6. Synthesis and crystallization
All experiments were performed under a dry N₂ atmosphere using standard Schlenk techniques. All solvents used in this study were freshly distilled over appropriate drying reagents prior to use. All starting materials were purchased commercially and used without further purification. The ¹H NMR spectrum was recorded on a JEOL 400 MHz spectrometer. The ligand, 2,6-difluoro-2,3′-bipyridine (Park et al., 2015) was synthesized according to the previous report. The title compound was synthesized as follows: the ligand (0.075 g, 0.39 mmol) in THF (2 ml) was added to Ag(CF₃SO₃) (0.47 g, 1.0 mmol) in MeOH (2 ml) in the dark at room temperature and the mixture was stirred for 10 min. After that, the mixture was slowly evaporated in the air and a dark environment to obtain crystals suitable for X-ray crystallographic analysis.

¹H NMR (400 MHz, CD₃CN) δ 8.67 (d, J = 4.4 Hz, 1H), 8.62 (td, J = 8.8, 1.2 Hz, 1H), 7.88–7.80 (m, 2H), 7.37–7.34 (m, 1H), 7.08 (dd, J = 9.2, 3.6 Hz, 1H). ¹³C NMR (376 MHz, CD₃CN) δ −69.7, −71.8, 79.1. Analysis calculated for C₂₁H₁₂F₇N₄O₃SAg: C 39.33; H 1.89; N 8.74%; found: C 39.44, H 1.86, N 8.70%.

7. Refinement
Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were positioned geometrically and refined using a riding model: C—H = 0.95 Å with Uiso(H) = 1.2Ueq(C).

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Synthesis, crystal structure and photophysical properties of bis[2,6-difluoro-3-(pyridin-2-yl)pyridine-κN](trifluoromethanesulfonato-κO)silver(I)

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Crystal data

\[\text{[Ag(CF}_3\text{O}_3\text{S})(\text{C}_10\text{H}_6\text{F}_2\text{N}_2)\text{]}}\]

\(M_r = 641.28\)

Triclinic, \(P\bar{1}\)

\(a = 9.0627 (2) \text{ Å}\)

\(b = 10.9637 (3) \text{ Å}\)

\(c = 12.5727 (3) \text{ Å}\)

\(α = 82.4508 (11)°\)

\(β = 73.7215 (11)°\)

\(γ = 71.5490 (11)°\)

\(V = 1136.26 (5) \text{ Å}^3\)

\(Z = 2\)

\(F(000) = 632\)

\(D_\text{x} = 1.874 \text{ Mg m}^{-3}\)

Mo \(K\alpha\) radiation, \(λ = 0.71073 \text{ Å}\)

Cell parameters from 9858 reflections

\(θ = 2.5–28.3°\)

\(μ = 1.07 \text{ mm}^{-1}\)

\(T = 193 \text{ K}\)

Block, colourless

\(0.38 \times 0.33 \times 0.32 \text{ mm}\)

Data collection

Bruker APEX II CCD
diffractometer

\(φ\) and \(ω\) scans

Absorption correction: multi-scan

(SADABS; Bruker, 2014)

\(T_{\text{min}} = 0.610, T_{\text{max}} = 0.746\)

19973 measured reflections

5623 independent reflections

5262 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.029\)

\(θ_{\text{max}} = 28.3°, θ_{\text{min}} = 2.5°\)

\(h = -12→11\)

\(k = -14→14\)

\(l = -16→14\)

Refinement

Refinement on \(F^2\)

Least-squares matrix: full

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

\(wR(F^2) = 0.067\)

\(S = 1.12\)

5623 reflections

334 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Hydrogen site location: inferred from neighbour sites

H-atom parameters constrained

\(w = 1/[(σ^2(F_c^2) + (0.0356P)^2 + 0.2813P)]\)

where \(P = (F_c^2 + 2F_s^2)/3\)

\((Δ/σ)_{\text{max}} = 0.001\)

\(Δρ_{\text{max}} = 0.33 \text{ e Å}^{-3}\)

\(Δρ_{\text{min}} = -0.76 \text{ e Å}^{-3}\)
Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|    | x     | y     | z     | Uiso/eq |
|----|-------|-------|-------|---------|
| Ag1| 0.39687 (2) | 0.11579 (2) | 0.28356 (2) | 0.02967 (5) |
| S  | 0.58088 (5)  | −0.20353 (4) | 0.43046 (4)  | 0.02529 (9)  |
| O1 | 0.47418 (19) | −0.09076 (14) | 0.39174 (14) | 0.0444 (4)  |
| O2 | 0.54144 (16) | −0.22732 (14) | 0.54886 (11) | 0.0356 (3)  |
| O3 | 0.74849 (17) | −0.22309 (15) | 0.37857 (12) | 0.0400 (3)  |
| C21| 0.5358 (3)  | −0.3333 (2)  | 0.38115 (18) | 0.0392 (4)  |
| F5 | 0.5511 (2)  | −0.31983 (18) | 0.27233 (12) | 0.0745 (5)  |
| F6 | 0.6317 (2)  | −0.44672 (13) | 0.40282 (16) | 0.0701 (5)  |
| F7 | 0.38549 (17) | −0.33477 (14) | 0.42807 (13) | 0.0562 (4)  |
| F1 | 0.7648 (2)  | −0.33112 (13) | −0.01970 (14) | 0.0698 (5)  |
| F2 | 0.63399 (17) | 0.08741 (13)  | −0.11751 (10) | 0.0460 (3)  |
| N1 | 0.7033 (2)  | −0.12143 (18) | −0.06736 (14) | 0.0414 (4)  |
| N2 | 0.57260 (17) | 0.21084 (14)  | 0.17341 (12)  | 0.0249 (3)  |
| C1 | 0.7501 (3)  | −0.21327 (19) | 0.00565 (19)  | 0.0430 (5)  |
| C2 | 0.7813 (3)  | −0.1947 (2)   | 0.10241 (18)  | 0.0414 (5)  |
| H2 | 0.8198     | −0.2652      | 0.1500        | 0.050*      |
| C3 | 0.7538 (2)  | −0.06916 (18) | 0.12668 (16)  | 0.0334 (4)  |
| H3 | 0.7695     | 0.03051      | 0.1940        | 0.040*      |
| C4 | 0.7031 (2)  | 0.03212 (17)  | 0.05317 (14)  | 0.0277 (3)  |
| C5 | 0.6836 (2)  | −0.00397 (19) | −0.04231 (15) | 0.0324 (4)  |
| C6 | 0.6718 (2)  | 0.16833 (17)  | 0.07537 (14)  | 0.0274 (3)  |
| C7 | 0.7452 (3)  | 0.2481 (2)    | −0.00157 (18) | 0.0443 (5)  |
| H7 | 0.8157     | 0.2158       | −0.0700       | 0.053*      |
| C8 | 0.7154 (3)  | 0.3738 (2)    | 0.0216 (2)    | 0.0518 (6)  |
| H8 | 0.7646     | 0.4294       | −0.0304       | 0.062*      |
| C9 | 0.6128 (3)  | 0.4179 (2)    | 0.12161 (18)  | 0.0408 (5)  |
| H9 | 0.5885     | 0.5049       | 0.1393        | 0.049*      |
| C10| 0.5462 (2)  | 0.33348 (18)  | 0.19542 (16)  | 0.0313 (4)  |
| H10 | 0.4783  | 0.3635       | 0.2652        | 0.038*      |
| F3 | 0.13496 (19) | 0.67539 (12)  | 0.27171 (13)  | 0.0583 (4)  |
| F4 | −0.07604 (18) | 0.40180 (14)  | 0.17706 (12)  | 0.0545 (4)  |
| N3 | 0.0298 (2)  | 0.53662 (16)  | 0.22662 (15)  | 0.0401 (4)  |
| N4 | 0.14448 (16) | 0.10066 (14)  | 0.33810 (12)  | 0.0244 (3)  |
| C11| 0.1051 (2)  | 0.56069 (17)  | 0.29307 (18)  | 0.0381 (4)  |
| C12| 0.1546 (2)  | 0.48149 (18)  | 0.37758 (17)  | 0.0348 (4)  |
| H12| 0.2070     | 0.5058       | 0.4234        | 0.042*      |
| C13| 0.1239 (2)  | 0.36367 (17)  | 0.39263 (15)  | 0.0280 (3)  |
| H13| 0.1566     | 0.3044       | 0.4499        | 0.034*      |
| C14| 0.04554 (19) | 0.33106 (16)  | 0.32476 (14)  | 0.0259 (3)  |
### Atomic displacement parameters (Å²)

|   | $U^{11}$   | $U^{22}$   | $U^{33}$   | $U^{12}$   | $U^{13}$   | $U^{23}$   |
|---|------------|------------|------------|------------|------------|------------|
| Ag1| 0.02256 (8)| 0.02807 (8)| 0.03687 (9)| −0.01100 (5)| −0.00184 (5)| 0.00012 (5) |
| S1 | 0.0262 (2) | 0.02496 (19)| 0.0277 (2) | −0.00994 (16)| −0.01063 (16)| 0.00272 (15) |
| O1 | 0.0493 (9) | 0.0297 (7)  | 0.0602 (10)| −0.0111 (6) | −0.0309 (8) | 0.0128 (7)  |
| O2 | 0.0324 (7) | 0.0467 (8)  | 0.0274 (7) | −0.0118 (6) | −0.0074 (5) | −0.0002 (6) |
| O3 | 0.0313 (7) | 0.0560 (9)  | 0.0356 (7) | −0.0211 (6) | −0.0045 (6) | −0.0003 (6) |
| C21| 0.0471 (11)| 0.0352 (10)| 0.0392 (11)| −0.0220 (9) | −0.0053 (9) | −0.0027 (8) |
| F5 | 0.1206 (15)| 0.0919 (12)| 0.0389 (8) | −0.0719 (12)| −0.0136 (9) | −0.0112 (8) |
| F6 | 0.0722 (10)| 0.0270 (6)  | 0.1019 (14)| −0.0094 (7) | −0.0113 (9) | −0.0083 (7) |
| F7 | 0.0522 (8) | 0.0609 (9)  | 0.0689 (10)| −0.0393 (7) | −0.0093 (7) | −0.0056 (7) |
| F1 | 0.0974 (13)| 0.0359 (7)  | 0.0692 (10)| −0.0239 (8) | 0.0022 (9) | −0.0199 (7) |
| F2 | 0.0640 (8) | 0.0479 (7)  | 0.0289 (6) | −0.0161 (6) | −0.0189 (6) | 0.0037 (5)  |
| N1 | 0.0518 (11)| 0.0434 (10)| 0.0307 (9) | −0.0190 (8) | −0.0027 (7) | −0.0116 (7) |
| N2 | 0.0255 (7) | 0.0279 (7)  | 0.0233 (7) | −0.0113 (6) | −0.0053 (5) | −0.0013 (5) |
| C1 | 0.0499 (12)| 0.0298 (10)| 0.0431 (12)| −0.0127 (9) | 0.0041 (9) | −0.0126 (8) |
| C2 | 0.0435 (11)| 0.0324 (10)| 0.0394 (11)| −0.0061 (8) | −0.0046 (9) | 0.0026 (8)  |
| C3 | 0.0355 (10)| 0.0351 (9)  | 0.0281 (9) | −0.0097 (8) | −0.0075 (7) | 0.0003 (7)  |
| C4 | 0.0286 (8) | 0.0309 (8)  | 0.0229 (8) | −0.0108 (7) | −0.0028 (6) | −0.0022 (7) |
| C5 | 0.0373 (10)| 0.0373 (10)| 0.0228 (8) | −0.0135 (8) | −0.0047 (7) | −0.0017 (7) |
| C6 | 0.0299 (8) | 0.0311 (8)  | 0.0232 (8) | −0.0128 (7) | −0.0061 (7) | −0.0003 (6) |
| C7 | 0.0578 (13)| 0.0455 (11)| 0.0290 (10)| −0.0285 (10)| 0.0060 (9) | −0.0039 (8) |
| C8 | 0.0740 (16)| 0.0464 (12)| 0.0401 (12)| −0.0392 (12)| 0.0005 (11)| 0.0017 (10) |
| C9 | 0.0546 (13)| 0.0319 (9)  | 0.0409 (11)| −0.0217 (9) | −0.0095 (9) | −0.0024 (8) |
| C10| 0.0337 (9) | 0.0309 (9)  | 0.0317 (9) | −0.0126 (7) | −0.0072 (7) | −0.0046 (7) |
| F3 | 0.0732 (10)| 0.0287 (6)  | 0.0657 (9) | −0.0207 (6) | −0.0007 (7) | 0.0006 (6)  |
| F4 | 0.0618 (9) | 0.0655 (9)  | 0.0485 (8) | −0.0220 (7) | −0.0370 (7) | 0.0138 (7)  |
| N3 | 0.0418 (9) | 0.0312 (8)  | 0.0376 (9) | −0.0032 (7) | −0.0069 (7) | 0.0060 (7)  |
| N4 | 0.0206 (6) | 0.0277 (7)  | 0.0248 (7) | −0.0079 (5) | −0.0052 (5) | −0.0006 (5) |
| C11| 0.0393 (10)| 0.0217 (8)  | 0.0430 (11)| −0.0070 (7) | 0.0041 (8) | −0.0032 (8) |
| C12| 0.0344 (10)| 0.0314 (9)  | 0.0384 (10)| −0.0093 (7) | −0.0060 (8) | −0.0089 (8) |
| C13| 0.0257 (8) | 0.0286 (8)  | 0.0284 (9) | −0.0055 (6) | −0.0071 (7) | −0.0019 (7) |
| C14| 0.0205 (7) | 0.0268 (8)  | 0.0275 (8) | −0.0030 (6) | −0.0057 (6) | −0.0016 (6) |
| C15| 0.0308 (9) | 0.0368 (10)| 0.0306 (9) | −0.0044 (7) | −0.0108 (7) | 0.0010 (8)  |
| C16| 0.0226 (8) | 0.0303 (8)  | 0.0228 (8) | −0.0074 (6) | −0.0063 (6) | −0.0015 (6) |
| C17| 0.0219 (8) | 0.0396 (10)| 0.0364 (10)| −0.0064 (7) | −0.0077 (7) | −0.0069 (8) |
### Geometric parameters (Å, °)

| Bond/Angle | Distance/Angle |
|------------|----------------|
| Ag1—N2     | 2.2305 (14)    |
| Ag1—N4     | 2.2496 (14)    |
| Ag1—O1     | 2.4879 (13)    |
| S1—O1      | 1.4317 (14)    |
| S1—O3      | 1.4331 (14)    |
| S1—O2      | 1.4389 (14)    |
| S1—C21     | 1.821 (2)      |
| C21—F6     | 1.317 (3)      |
| C21—F7     | 1.329 (2)      |
| C21—F5     | 1.329 (3)      |
| F1—C1      | 1.338 (2)      |
| F2—C5      | 1.343 (2)      |
| N1—C5      | 1.311 (3)      |
| N1—C1      | 1.314 (3)      |
| N2—C10     | 1.341 (2)      |
| N2—C6      | 1.345 (2)      |
| C1—C2      | 1.374 (3)      |
| C2—C3      | 1.379 (3)      |
| C2—H2      | 0.9500         |
| C3—C4      | 1.394 (3)      |
| C3—H3      | 0.9500         |
| C4—C5      | 1.385 (2)      |
| C4—C6      | 1.478 (2)      |
| C6—C7      | 1.389 (3)      |
| C7—C8      | 1.372 (3)      |
| C7—H7      | 0.9500         |
| N2—Ag1—N4  | 148.65 (5)     |
| N2—Ag1—O1  | 124.02 (5)     |
| N4—Ag1—O1  | 86.55 (5)      |
| O1—S1—O3   | 115.37 (9)     |
| O1—S1—O2   | 114.61 (9)     |
| O3—S1—O2   | 115.25 (8)     |
| O1—S1—C21  | 102.70 (10)    |
| O3—S1—C21  | 103.67 (10)    |
| O2—S1—C21  | 102.70 (9)     |
| S1—O1—Ag1  | 155.68 (10)    |
| F6—C21—F7  | 107.60 (17)    |
| F6—C21—F5  | 108.1 (2)      |
| F7—C21—F5  | 106.53 (18)    |
| F6—C21—S1  | 111.59 (15)    |
| F7—C21—S1  | 111.55 (15)    |

**Supporting information**

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F5—C21—S1 111.22 (14)  C11—C12—C13 116.10 (18)
C5—N1—C1 115.27 (18)  C11—C12—H12 121.9
C10—N2—C6 118.01 (15)  C13—C12—H12 121.9
C10—N2—Ag1 114.60 (12)  C12—C13—C14 120.70 (17)
C6—N2—Ag1 125.25 (11)  C12—C13—H12 121.9
N1—C1—F1 114.4 (2)  C13—C12—H12 121.9
N1—C1—C2 126.05 (19)  C15—C14—C16 123.52 (16)
F1—C1—C2 119.5 (2)  C15—C14—C13 114.98 (16)
C1—C2—C3 116.39 (19)  C15—C14—C17 120.3
C1—C2—H2 121.8  N3—C15—F4 114.67 (16)
C3—C2—H2 121.8  N3—C15—C14 114.67 (16)
C2—C3—C4 120.53 (18)  C12—C13—C14 120.3
C2—C3—H3 119.7  N4—C16—C17 118.84 (17)
C4—C3—H3 119.7  N4—C16—C14 118.84 (17)
C5—C4—C3 115.13 (17)  C16—C17—C18 119.40 (17)
C5—C4—C6 122.25 (16)  C16—C17—H17 120.3
C3—C4—C6 122.62 (16)  C18—C17—C16 119.40 (17)
N1—C5—F2 114.19 (16)  C18—C17—H17 120.3
N1—C5—C4 126.55 (18)  C16—C17—H17 120.3
F2—C5—C4 119.21 (17)  C19—C18—C17 119.40 (17)
N2—C6—C7 121.54 (17)  C19—C18—H18 120.6
N2—C6—C4 117.53 (15)  C19—C18—H18 120.6
C7—C6—C4 120.92 (17)  C16—C17—C18 120.6
C7—C6—C7 119.7 (2)  C20—C19—C18 118.87 (17)
C8—C7—C6 120.1  C20—C19—H18 120.6
C8—C7—H7 120.1  N4—C20—C19 123.19 (16)
C6—C7—H7 120.1  N4—C20—H20 123.19 (16)
C7—C8—C9 118.86 (19)  C19—C20—H20 123.19 (16)

O3—S1—O1—Ag1 −5.5 (3)  C4—C6—C7—C8 −179.3 (2)
O2—S1—O1—Ag1 131.9 (2)  C4—C6—C7—C8 0.1 (4)
C21—S1—O1—Ag1 −117.5 (3)  C6—N2—C10—C9 −162.77 (16)
O1—S1—C21—F6 175.69 (16)  Ag1—N2—C10—C9 1.5 (3)
O3—S1—C21—F6 55.24 (17)  Ag1—N2—C10—C9 −162.77 (16)
O2—S1—C21—F6 −65.08 (17)  C8—C9—C10—N2 2.0 (3)
O1—S1—C21—F7 −63.92 (17)  C15—N3—C11—F3 179.02 (17)
O3—S1—C21—F7 175.64 (15)  C15—N3—C11—C12 0.4 (3)
O2—S1—C21—F7 55.32 (17)  C15—N3—C11—C12 1.2 (3)
O1—S1—C21—F5 54.86 (19)  F3—C11—C12—C13 −178.21 (17)
O3—S1—C21—F5 −65.58 (18)  F3—C11—C12—C13 1.5 (3)
O2—S1—C21—F5 174.10 (16)  C11—C12—C13—C14 −0.6 (3)
C5—N1—C1—F1 178.08 (19)  C12—C13—C14—C15 0.6 (3)
C5—N1—C1—C2 −1.0 (3)  C12—C13—C14—C16 178.08 (17)
N1—C1—C2—C3 3.0 (4)  C11—N3—C15—C14 1.1 (3)
F1—C1—C2—C3 −175.97 (19)  C13—C14—C15—N3 1.5 (3)
C1—C2—C3—C4 −2.4 (3)  C16—C14—C15—F4 −177.11 (18)
C2—C3—C4—C5 0.1 (3)  C13—C14—C15—F4 179.13 (17)
C2—C3—C4—C6 179.92 (18)  C16—C14—C15—F4 2.2 (3)
C1—N1—C5—F2 −179.29 (18)  C20—N4—C16—C17 −0.1 (3)
C1—N1—C5—C4  
C3—C4—C5—N1  
C6—C4—C5—N1  
C3—C4—C5—F2  
C6—C4—C5—F2  
Ag1—N2—C6—N2  
Ag1—N2—C6—C4  
C5—C4—C6—N2  
C3—C4—C6—N2  
C5—C4—C6—C7  
C3—C4—C6—C7  
N2—C6—C7—C8  

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|------|-------|-------|--------|
| C10—H10···O2i | 0.95 | 2.60 | 3.239 (2) | 125 |
| C13—H13···O2i | 0.95 | 2.60 | 3.173 (2) | 119 |
| C13—H13···O3i | 0.95 | 2.50 | 3.400 (2) | 159 |
| C19—H19···O3i | 0.95 | 2.53 | 3.294 (2) | 137 |
| C20—H20···O1 | 0.95 | 2.55 | 3.197 (2) | 126 |

Symmetry codes: (i) −x+1, −y, −z+1; (ii) x−1, y, z.