

A dinuclear silver(I) complex of 6-phenyl-2,2':6',2''-terpyridine

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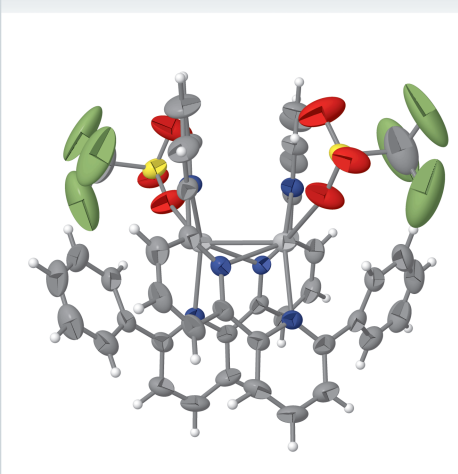
Keywords: argentophilic interaction; crystal structure; dinuclear complex; π - π stacking; silver(I); terpyridine.

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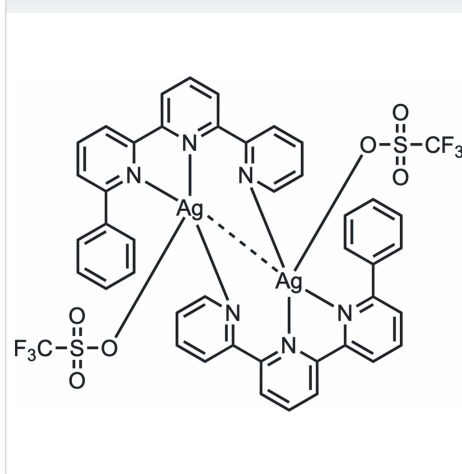
Structural data: full structural data are available from iucrdata.iucr.org

A dinuclear silver(I) complex of 6-phenyl-2,2':6',2''-terpyridine, bis(μ -6-phenyl-2,2':6',2''-terpyridine)bis[(trifluoromethanesulfonato)silver(I)], $[\text{Ag}_2(\text{C}_{21}\text{H}_{15}\text{N}_3)(\text{CF}_3\text{SO}_3)_2]$, was obtained by crystallization with silver trifluoromethanesulfonate and characterized by single-crystal X-ray diffraction. Two symmetry-related terpyridine ligands bridge two Ag^{I} ions. The Ag^{I} ion has a highly distorted four-coordinate N_3O environment comprising three pyridyl N atoms and one trifluoromethanesulfonate O atom. The intramolecular $\text{Ag}\cdots\text{Ag}$ separation of 2.8501 (8) Å is consistent with an argentophilic interaction. An intramolecular phenyl-pyridyl π - π contact is also present. The structure demonstrates that a single phenyl substituent at the 6-position is compatible with ligand bridging and the formation of a short $\text{Ag}\cdots\text{Ag}$ contact.

3D view



Chemical scheme



Structure description

Ag^{I} complexes of 2,2':6',2''-terpyridine (tpy) exhibit diverse coordination modes and solvent-dependent nuclearity. Crystallization from acetonitrile (MeCN) affords approximately square-planar $[\text{Ag}(\text{tpy})(\text{MeCN})]^+$ units, which associate into dimers through an $\text{Ag}\cdots\text{Ag}$ contact of 3.170 Å (Constable *et al.*, 1998*a,b*). Chiral tpy derivatives form mononuclear acetonitrile complexes but favour dinuclear double helicates in less coordinating solvents. These helicates contain intramolecular $\text{Ag}\cdots\text{Ag}$ contacts of 2.914–2.940 Å and associate into tetranuclear aggregates through additional $\text{Ag}\cdots\text{Ag}$ interactions (Baum *et al.*, 1998). Similarly, 6,6''-dimethyl-tpy forms dinuclear double helicates with $\text{Ag}\cdots\text{Ag}$ distances of 2.930–2.970 Å. Their structures depend on the counter-ion: nitrate and trifluoromethanesulfonate produce asymmetric helicates with one bridging central pyridine N atom, whereas BF_4^- and ClO_4^- give more symmetrical structures with both central N atoms bridging the Ag pair (Fik *et al.*, 2014). Dinuclear Ag-tpy units can also form extended chains with gold complexes through $\text{Ag}\cdots\text{Au}$ and $\text{Au}\cdots\text{Au}$ interactions (Gil-Moles *et al.*, 2017). Solution studies support mononuclear $[\text{Ag}(\text{tpy})_2]^+$

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C3-H3\cdots O2^i$	0.93	2.43	3.273 (6)	150
$C9-H9\cdots O2^{ii}$	0.93	2.58	3.278 (5)	132
$C9-H9\cdots O1^{ii}$	0.93	2.65	3.315 (5)	130

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

species. Thermodynamic measurements in dimethyl sulfoxide (DMSO) suggest five-coordinate bonds with one unbound pyridine ring (Del Piero *et al.*, 2007), while selective formation of an $[Ag(tpy)_2]^+$ unit was demonstrated in an Ag^I capture-release system (Paul *et al.*, 2019).

Against this background, we report the crystal structure of the trifluoromethanesulfonate salt of a dinuclear Ag^I complex containing 6-phenyl-2,2':6',2''-terpyridine (6-Phtpy). The asymmetric unit contains one 6-Phtpy ligand, one Ag^I ion and one trifluoromethanesulfonate anion. Two symmetry-related 6-Phtpy ligands bridge two central Ag^I ions in a helical arrangement, forming a chiral dinuclear complex (Fig. 1). A crystallographic twofold rotation axis passes through the midpoint of, and perpendicular to, the $Ag\cdots Ag$ vector. Each Ag^I centre has a highly distorted four-coordinate N_3O environment containing one pyridyl N atom from one ligand, two pyridyl N atoms from the other ligand and one trifluoromethanesulfonate O atom. The $Ag1-N1$, $Ag1-N2^i$ and $Ag1-N3^i$ distances are 2.240 (3), 2.412 (3) and 2.330 (2) Å, respectively, and $Ag1-O1$ is 2.578 (4) Å [symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$]. The intramolecular $Ag1\cdots Ag1^i$ distance of 2.8500 (6) Å is consistent with an argentophilic interaction (Schmidbaur & Schier, 2015). The ligand adopts a nonplanar conformation. The dihedral angles between the N1- and N2-containing pyridine rings and between the N2- and N3-containing rings are 43.85 (16) and 16.62 (13)°, respectively. The phenyl substituent is inclined by 38.65 (16)° to the adja-

cent N3-containing pyridine ring. Within the dinuclear complex, the phenyl ring and a symmetry-related $N2^i$ -containing pyridine ring form a $\pi\cdots\pi$ contact, with a centroid-centroid distance of 3.750 (3) Å and an interplanar angle of 10.58 (15)°.

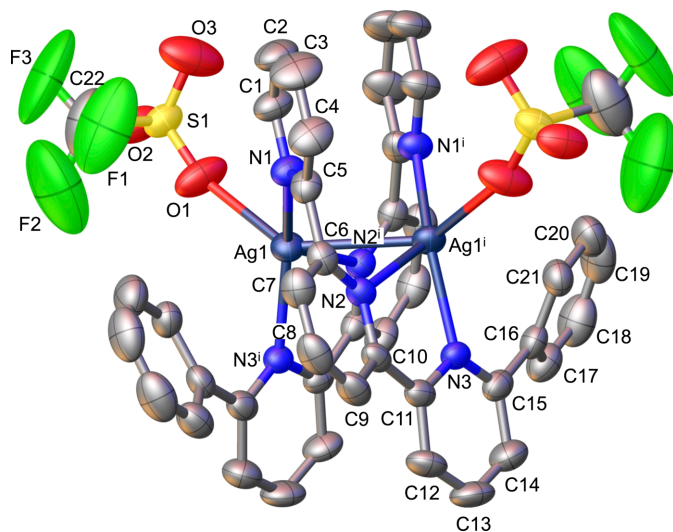
The dinuclear framework resembles that of $Ag_2(tpy)_2$, which contains bridging unsubstituted tpy ligands and weak $Ag-O$ interactions with trifluoromethanesulfonate anions (Gil-Moles *et al.*, 2017). The reported $Ag_2(tpy)_2$ complex has an $Ag\cdots Ag$ contact of 3.1698 (12) Å. The related $[Ag(dptpy)(MeCN)]^+$ complex, with $dptpy = 6,6''$ -diphenyl-tpy, is mononuclear and has no short $Ag\cdots Ag$ contact; the shortest separation is 5.656 Å (Constable *et al.*, 1998). Thus, a single phenyl substituent at the 6-position is compatible with ligand bridging and a short intramolecular $Ag\cdots Ag$ contact.

The crystal packing features offset $\pi\cdots\pi$ stacking between the central pyridine rings of neighbouring complexes, together with weak $C-H\cdots O$ contacts involving the trifluoromethanesulfonate anions (Fig. 2). The central pyridine rings of neighbouring complexes of opposite handedness, related by inversion (symmetry operation: $-x, -y + 1, -z + 2$), are parallel, with a centroid-centroid distance of 3.879 (3) Å. The $C3-H3\cdots O2$ contact has a $C\cdots O$ distance of 3.273 (6) Å and a $C-H\cdots O$ angle of 150°. The H9 atom forms a bifurcated contact with O2 and O1, with $C9\cdots O$ distances of 3.278 (5) and 3.315 (5) Å, and angles of 132 and 130°, respectively. Details of the weak $C-H\cdots O$ contacts are given in Table 1.

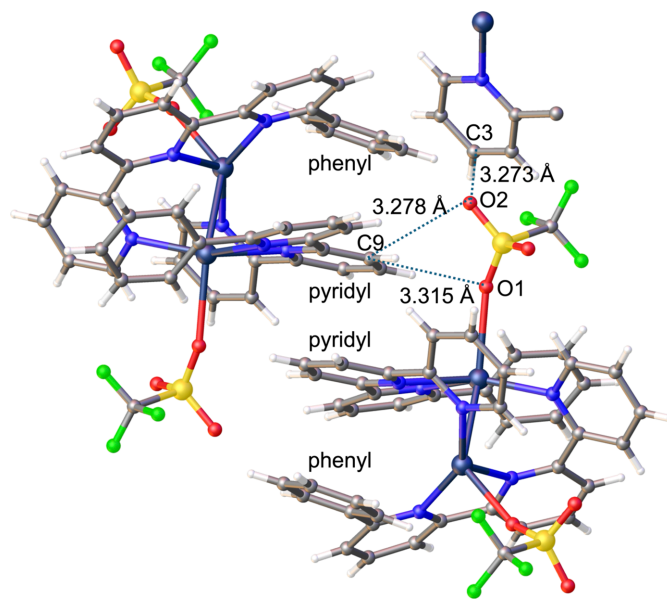
Synthesis and crystallization

The synthetic route to 6-Phtpy is shown in Fig. 3.

6-Bromo-2,2':6',2''-terpyridine (2). The known compound **2** was prepared according to literature procedures (Derrick *et al.*, 2020; Stefankiewicz *et al.*, 2013) using solvents without

**Figure 1**

The molecular structure of the dinuclear Ag^I complex of 6-Phtpy. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, y, -z + \frac{3}{2}$.]

**Figure 2**

The crystal packing of the dinuclear complex, showing phenyl-pyridyl-pyridyl-phenyl $\pi\cdots\pi$ stacking and $C-H\cdots O$ contacts (labelled distances are $C\cdots O$ separations).

prior drying and with the purification procedure modified as follows. The product was purified by column chromatography (SiO_2 , CHCl_3), followed by gel permeation chromatography (GPC), to afford compound **2** in 45% yield.

6-Phenyl-2,2':6',2''-terpyridine (6-Phtpy). 6-Phtpy is a known compound (Constable *et al.*, 1999), but its synthesis from compound **2** has not been reported previously. Compound **2** (168 mg, 0.537 mmol), phenylboronic acid pinacol ester (115 mg, 0.563 mmol), $\text{Pd}(\text{PPh}_3)_4$ (65 mg, 0.056 mmol) and Na_2CO_3 (286 mg, 2.69 mmol) were added to a mixture of H_2O (1.3 ml), toluene (5.0 ml) and EtOH (2.5 ml). The mixture was degassed by three freeze–pump–thaw cycles and refluxed under N_2 for 24 h. The solvents were removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 . The solution was washed with water three times, and the organic layer was concentrated under reduced pressure. The crude product was washed with MeOH and collected by filtration. The resulting solid was dissolved in CHCl_3 , and the solution was filtered. The filtrate was concentrated under reduced pressure to afford 6-Phtpy as a white solid (yield: 142 mg, 0.458 mmol, 85%).

Crystallization. 6-Phtpy and silver(I) trifluoromethanesulfonate (AgOTf) were dissolved in acetone (10 ml) in a 10 ml vial, giving a concentration of 2.5 mM for each component. Slow evaporation at room temperature under ambient conditions afforded colourless needle-shaped crystals after 44 d. A block-shaped specimen was cut from a needle for single-crystal X-ray diffraction.

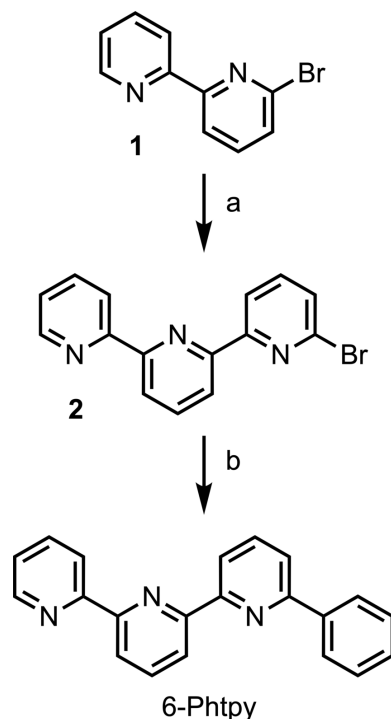


Figure 3

Synthetic route to 6-Phtpy. Reagents and conditions: (a) i) hexamethylditin, $\text{Pd}(\text{PPh}_3)_4$, DME, reflux, 18 h; ii) 2,6-dibromopyridine, $\text{Pd}(\text{PPh}_3)_4$, toluene, reflux, 24 h, 45%; (b) phenylboronic acid pinacol ester, $\text{Pd}(\text{PPh}_3)_4$, Na_2CO_3 , H_2O , toluene, EtOH, reflux, 24 h, 85%.

Table 2

Experimental details.

Crystal data	
Chemical formula	$[\text{Ag}_2(\text{C}_{21}\text{H}_{15}\text{N}_3)(\text{CF}_3\text{O}_3\text{S})_2]$
M_r	1132.60
Crystal system, space group	Orthorhombic, <i>Pbcn</i>
Temperature (K)	293
a, b, c (Å)	21.3041 (10), 11.7253 (4), 17.3544 (8)
V (Å ³)	4335.1 (3)
Z	4
Radiation type	$\text{Mo K}\alpha$
μ (mm ^{−1})	1.08
Crystal size (mm)	0.35 × 0.1 × 0.06
Data collection	
Diffractometer	Rigaku XtaLAB Mini II
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2022)
$T_{\min}, T_{\max}$	0.700, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26970, 6431, 3745
R_{int}	0.038
$(\sin \theta/\lambda)_{\text{max}}$ (Å ^{−1})	0.718
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.047, 0.159, 0.92
No. of reflections	6431
No. of parameters	298
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ^{−3})	0.57, −0.79

Computer programs: *CrysAlis PRO* (Rigaku OD, 2022), *SHELXT2018* (Sheldrick, 2015a), *SHELXL2025* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Reflections 200 and 110 were omitted because they were considered to be affected by the beamstop. The trifluoromethanesulfonate CF_3 group exhibits large anisotropic displacement parameters. Inspection of the difference electron-density map revealed no significant residual features near this group.

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Author contributions: Yuto Nakaie: investigation, writing – original draft. Tomoya Abe: investigation. Yosuke Hosoya: supervision. Kosuke Sugawa: supervision. Joe Otsuki: conceptualization, supervision, writing – review and editing.

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References

- Constable, E. C., Baum, G., Bill, E., Dyson, R., van Eldik, R., Fenske, D., Kaderli, S., Morris, D., Neubrand, A., Neuburger, M., Smith, D. R., Wieghardt, K., Zehnder, M. & Zuberbühler, A. D. (1999). *Chem. Eur. J.* **5**, 498–508.
- Baum, G., Constable, E. C., Fenske, D., Housecroft, C. E. & Kulke, T. (1998). *Chem. Commun.* pp. 2659–2660.

- Constable, E. C., Edwards, A. J., Haire, G. R., Hannon, M. J. & Raithby, P. R. (1998a). *Polyhedron* **17**, 243–253.
- Constable, E. C., Housecroft, D. F. C. E. & Kulke, T. (1998b). *Chem. Commun.* pp. 2659–2660.
- Del Piero, S., Fedele, R., Melchior, A., Portanova, R., Tolazzi, M. & Zangrando, E. (2007). *Inorg. Chem.* **46**, 4683–4691.
- Derrick, J. S., Loipersberger, M., Chatterjee, R., Iovan, D. A., Smith, P. T., Chakarawet, K., Yano, J., Long, J. R., Head-Gordon, M. & Chang, C. J. (2020). *J. Am. Chem. Soc.* **142**, 20489–20501.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Fik, M. A., Gorczyński, A., Kubicki, M., Hnatejko, Z., Fedoruk-Wyszomirska, A., Wyszko, E., Giel-Pietraszuk, M. & Patroniak, V. (2014). *Eur. J. Med. Chem.* **86**, 456–468.
- Gil-Moles, M., Gimeno, M. C., López-de-Luzuriaga, J. M., Monge, M., Olmos, M. E. & Pascual, D. (2017). *Inorg. Chem.* **56**, 9281–9290.
- Paul, I., Mittal, N., De, S., Bolte, M. & Schmittl, M. (2019). *J. Am. Chem. Soc.* **141**, 5139–5143.
- Rigaku OD (2022). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
- Schmidbaur, H. & Schier, A. (2015). *Angew. Chem. Int. Ed.* **54**, 746–784.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Stefankiewicz, A. R., Wałęsa-Chorab, M., Harrowfield, J., Kubicki, M., Hnatejko, Z., Korabik, M. & Patroniak, V. (2013). *Dalton Trans.* **42**, 1743–1751.

full crystallographic data

IUCrData (2026). **11**, x261043 [https://doi.org/10.1107/S2414314626010436]

A dinuclear silver(I) complex of 6-phenyl-2,2':6',2''-terpyridine

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Bis(μ -6-phenyl-2,2':6',2''-terpyridine)bis[(trifluoromethanesulfonato)silver(I)]

Crystal data

[Ag₂(C₂₁H₁₅N₃)(CF₃O₃S)₂]

$M_r = 1132.60$

Orthorhombic, *Pbcn*

$a = 21.3041$ (10) Å

$b = 11.7253$ (4) Å

$c = 17.3544$ (8) Å

$V = 4335.1$ (3) Å³

$Z = 4$

$F(000) = 2256$

$D_x = 1.735$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5625 reflections

$\theta = 2.1$ – 24.4°

$\mu = 1.08$ mm⁻¹

$T = 293$ K

Block, colourless

$0.35 \times 0.1 \times 0.06$ mm

Data collection

Rigaku XtaLAB Mini II

diffractometer

Radiation source: fine-focus sealed X-ray tube,

Rigaku (Mo) X-ray Source

Graphite monochromator

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlis PRO; Rigaku OD, 2022)

$T_{\min} = 0.700$, $T_{\max} = 1.000$

26970 measured reflections

6431 independent reflections

3745 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.038$

$\theta_{\max} = 30.7^\circ$, $\theta_{\min} = 2.3^\circ$

$h = -30 \rightarrow 26$

$k = -16 \rightarrow 16$

$l = -24 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.047$

$wR(F^2) = 0.159$

$S = 0.92$

6431 reflections

298 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.57$ e Å⁻³

$\Delta\rho_{\min} = -0.79$ 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.

Refinement. H atoms were placed in calculated positions, with C–H = 0.93 Å, and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ag1	0.55847 (2)	0.37117 (2)	0.71012 (2)	0.04187 (12)
S1	0.63201 (6)	0.16608 (9)	0.55585 (6)	0.0504 (3)
O2	0.63818 (18)	0.1843 (3)	0.47493 (17)	0.0703 (10)
N2	0.52874 (14)	0.4296 (2)	0.86920 (16)	0.0349 (7)
N3	0.43146 (14)	0.5640 (2)	0.81989 (18)	0.0366 (7)
N1	0.57184 (17)	0.2271 (3)	0.79332 (17)	0.0424 (8)
O1	0.6101 (2)	0.2597 (3)	0.59889 (19)	0.0825 (12)
C5	0.57356 (19)	0.2413 (3)	0.8704 (2)	0.0428 (9)
C15	0.3861 (2)	0.6287 (3)	0.7889 (2)	0.0439 (9)
C16	0.33765 (19)	0.5713 (3)	0.7428 (3)	0.0447 (9)
C10	0.52524 (18)	0.5368 (3)	0.8959 (2)	0.0378 (8)
O3	0.6053 (3)	0.0596 (3)	0.5772 (2)	0.1148 (17)
C11	0.47793 (19)	0.6128 (3)	0.8607 (2)	0.0390 (8)
C6	0.57040 (18)	0.3592 (3)	0.9001 (2)	0.0401 (9)
C4	0.5773 (3)	0.1487 (4)	0.9198 (3)	0.0651 (14)
H4	0.578236	0.160036	0.972827	0.078*
C1	0.5747 (2)	0.1201 (3)	0.7656 (3)	0.0531 (11)
H1	0.573638	0.108782	0.712619	0.064*
C9	0.56347 (19)	0.5729 (4)	0.9560 (2)	0.0501 (11)
H9	0.560162	0.647151	0.974331	0.060*
C14	0.3842 (3)	0.7457 (4)	0.8025 (3)	0.0607 (13)
H14	0.351214	0.789498	0.783776	0.073*
C7	0.6099 (2)	0.3925 (4)	0.9606 (2)	0.0524 (11)
H7	0.638705	0.341642	0.981709	0.063*
C12	0.4795 (2)	0.7297 (3)	0.8721 (2)	0.0551 (12)
H12	0.512633	0.763195	0.898656	0.066*
C17	0.3135 (2)	0.6216 (4)	0.6760 (3)	0.0582 (12)
H17	0.327801	0.693085	0.660634	0.070*
C21	0.3146 (2)	0.4648 (4)	0.7633 (3)	0.0523 (10)
H21	0.328688	0.430119	0.808279	0.063*
C3	0.5797 (3)	0.0418 (4)	0.8908 (3)	0.0798 (17)
H3	0.581669	−0.020786	0.923677	0.096*
C20	0.2711 (2)	0.4099 (5)	0.7176 (3)	0.0697 (14)
H20	0.256916	0.337755	0.731366	0.084*
C8	0.6052 (2)	0.5010 (4)	0.9877 (3)	0.0558 (11)
H8	0.630689	0.525308	1.028020	0.067*
C18	0.2689 (3)	0.5661 (6)	0.6329 (3)	0.0784 (16)
H18	0.252173	0.601509	0.589576	0.094*
C2	0.5792 (3)	0.0269 (4)	0.8136 (3)	0.0674 (14)
H2	0.581911	−0.046140	0.792846	0.081*
C19	0.2489 (2)	0.4599 (6)	0.6529 (3)	0.0799 (16)
H19	0.220032	0.421740	0.622141	0.096*
C13	0.4315 (3)	0.7954 (4)	0.8438 (3)	0.0652 (14)
H13	0.431054	0.873627	0.852724	0.078*
F1	0.7124 (3)	0.1423 (6)	0.6626 (3)	0.207 (3)

F3	0.7404 (3)	0.0703 (7)	0.5574 (3)	0.214 (3)
C22	0.7109 (5)	0.1506 (10)	0.5893 (5)	0.129 (3)
F2	0.7406 (3)	0.2552 (8)	0.5666 (4)	0.250 (4)

Atomic displacement parameters ($\text{\AA}^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.0483 (2)	0.03713 (17)	0.04016 (18)	0.00238 (13)	−0.00214 (13)	0.00872 (11)
S1	0.0657 (7)	0.0467 (5)	0.0389 (6)	0.0138 (5)	−0.0019 (5)	−0.0025 (4)
O2	0.115 (3)	0.0550 (18)	0.0406 (17)	0.019 (2)	0.0045 (18)	−0.0009 (14)
N2	0.0374 (17)	0.0374 (15)	0.0298 (15)	−0.0032 (14)	−0.0029 (13)	−0.0024 (12)
N3	0.0409 (19)	0.0332 (15)	0.0356 (16)	0.0001 (13)	0.0039 (14)	−0.0032 (12)
N1	0.053 (2)	0.0381 (16)	0.0358 (17)	0.0046 (15)	0.0000 (14)	0.0043 (13)
O1	0.131 (4)	0.062 (2)	0.054 (2)	0.034 (2)	0.011 (2)	−0.0065 (16)
C5	0.041 (2)	0.047 (2)	0.040 (2)	0.0065 (17)	−0.0031 (17)	0.0083 (17)
C15	0.048 (2)	0.0402 (19)	0.044 (2)	0.0071 (18)	0.0108 (18)	0.0025 (16)
C16	0.036 (2)	0.049 (2)	0.049 (2)	0.0111 (18)	0.0039 (18)	−0.0010 (19)
C10	0.040 (2)	0.0407 (19)	0.0327 (18)	−0.0107 (17)	0.0041 (16)	−0.0069 (15)
O3	0.186 (5)	0.077 (3)	0.081 (3)	−0.052 (3)	0.022 (3)	0.002 (2)
C11	0.046 (2)	0.0348 (18)	0.036 (2)	−0.0051 (16)	0.0078 (16)	−0.0026 (14)
C6	0.039 (2)	0.050 (2)	0.0320 (19)	−0.0040 (17)	−0.0026 (15)	0.0033 (15)
C4	0.086 (4)	0.062 (3)	0.047 (3)	0.015 (3)	−0.008 (2)	0.017 (2)
C1	0.070 (3)	0.040 (2)	0.050 (2)	0.010 (2)	0.002 (2)	0.0018 (18)
C9	0.049 (3)	0.056 (2)	0.046 (2)	−0.017 (2)	−0.0024 (19)	−0.0128 (19)
C14	0.066 (3)	0.040 (2)	0.077 (3)	0.011 (2)	0.003 (3)	−0.002 (2)
C7	0.046 (2)	0.071 (3)	0.041 (2)	−0.001 (2)	−0.0093 (18)	0.001 (2)
C12	0.070 (3)	0.035 (2)	0.060 (3)	−0.014 (2)	−0.003 (2)	−0.0083 (18)
C17	0.058 (3)	0.060 (3)	0.057 (3)	0.016 (2)	0.002 (2)	0.006 (2)
C21	0.039 (2)	0.057 (3)	0.061 (3)	0.000 (2)	0.002 (2)	0.004 (2)
C3	0.117 (5)	0.053 (3)	0.070 (4)	0.019 (3)	−0.009 (3)	0.027 (3)
C20	0.048 (3)	0.075 (3)	0.086 (4)	−0.010 (3)	0.000 (3)	−0.009 (3)
C8	0.048 (3)	0.079 (3)	0.041 (2)	−0.018 (2)	−0.010 (2)	−0.006 (2)
C18	0.061 (4)	0.113 (5)	0.061 (3)	0.023 (4)	−0.013 (3)	−0.001 (3)
C2	0.086 (4)	0.038 (2)	0.078 (3)	0.014 (2)	0.005 (3)	0.005 (2)
C19	0.044 (3)	0.123 (5)	0.073 (4)	−0.001 (3)	−0.015 (3)	−0.025 (4)
C13	0.090 (4)	0.0279 (19)	0.078 (3)	0.002 (2)	0.003 (3)	−0.006 (2)
F1	0.163 (5)	0.365 (9)	0.092 (4)	0.131 (5)	−0.056 (3)	−0.014 (4)
F3	0.167 (5)	0.332 (8)	0.144 (5)	0.182 (6)	0.015 (4)	−0.002 (5)
C22	0.102 (7)	0.201 (10)	0.084 (6)	0.045 (7)	−0.001 (5)	0.003 (6)
F2	0.129 (5)	0.393 (12)	0.228 (7)	−0.107 (7)	−0.015 (5)	0.004 (7)

Geometric parameters ($\text{\AA}$, $^\circ$)

Ag1—Ag1 ⁱ	2.8501 (8)	C1—H1	0.9300
Ag1—N2 ⁱ	2.412 (3)	C1—C2	1.377 (6)
Ag1—N3 ⁱ	2.330 (3)	C9—H9	0.9300
Ag1—N1	2.240 (3)	C9—C8	1.343 (6)
Ag1—O1	2.578 (3)	C14—H14	0.9300

S1—O2	1.427 (3)	C14—C13	1.366 (7)
S1—O1	1.407 (3)	C7—H7	0.9300
S1—O3	1.421 (4)	C7—C8	1.361 (6)
S1—C22	1.786 (9)	C12—H12	0.9300
N2—C10	1.342 (4)	C12—C13	1.372 (6)
N2—C6	1.326 (5)	C17—H17	0.9300
N3—C15	1.342 (5)	C17—C18	1.373 (7)
N3—C11	1.345 (5)	C21—H21	0.9300
N1—C5	1.349 (5)	C21—C20	1.380 (7)
N1—C1	1.345 (5)	C3—H3	0.9300
C5—C6	1.476 (5)	C3—C2	1.353 (7)
C5—C4	1.386 (5)	C20—H20	0.9300
C15—C16	1.468 (6)	C20—C19	1.351 (7)
C15—C14	1.393 (5)	C8—H8	0.9300
C16—C17	1.399 (6)	C18—H18	0.9300
C16—C21	1.388 (6)	C18—C19	1.362 (8)
C10—C11	1.478 (5)	C2—H2	0.9300
C10—C9	1.389 (5)	C19—H19	0.9300
C11—C12	1.385 (5)	C13—H13	0.9300
C6—C7	1.402 (5)	F1—C22	1.277 (9)
C4—H4	0.9300	F3—C22	1.260 (9)
C4—C3	1.351 (7)	C22—F2	1.436 (11)
N2 ⁱ —Ag1—Ag1 ⁱ	66.66 (7)	N1—C1—C2	121.9 (5)
N2 ⁱ —Ag1—O1	92.60 (11)	C2—C1—H1	119.1
N3 ⁱ —Ag1—Ag1 ⁱ	100.90 (8)	C10—C9—H9	119.8
N3 ⁱ —Ag1—N2 ⁱ	70.59 (10)	C8—C9—C10	120.4 (4)
N3 ⁱ —Ag1—O1	106.58 (11)	C8—C9—H9	119.8
N1—Ag1—Ag1 ⁱ	78.35 (9)	C15—C14—H14	120.3
N1—Ag1—N2 ⁱ	132.85 (12)	C13—C14—C15	119.3 (5)
N1—Ag1—N3 ⁱ	149.76 (12)	C13—C14—H14	120.3
N1—Ag1—O1	92.64 (11)	C6—C7—H7	120.8
O1—Ag1—Ag1 ⁱ	137.45 (10)	C8—C7—C6	118.4 (4)
O2—S1—C22	104.4 (3)	C8—C7—H7	120.8
O1—S1—O2	115.9 (2)	C11—C12—H12	120.4
O1—S1—O3	114.4 (3)	C13—C12—C11	119.1 (4)
O1—S1—C22	102.7 (4)	C13—C12—H12	120.4
O3—S1—O2	115.2 (2)	C16—C17—H17	119.8
O3—S1—C22	101.7 (4)	C18—C17—C16	120.3 (5)
C10—N2—Ag1 ⁱ	114.9 (2)	C18—C17—H17	119.8
C6—N2—Ag1 ⁱ	124.7 (2)	C16—C21—H21	119.7
C6—N2—C10	118.7 (3)	C20—C21—C16	120.6 (5)
C15—N3—Ag1 ⁱ	121.7 (3)	C20—C21—H21	119.7
C15—N3—C11	120.1 (3)	C4—C3—H3	120.4
C11—N3—Ag1 ⁱ	117.6 (2)	C4—C3—C2	119.3 (4)
C5—N1—Ag1	123.3 (3)	C2—C3—H3	120.4
C1—N1—Ag1	118.6 (3)	C21—C20—H20	119.7
C1—N1—C5	117.9 (4)	C19—C20—C21	120.7 (5)

S1—O1—Ag1	159.1 (2)	C19—C20—H20	119.7
N1—C5—C6	117.4 (3)	C9—C8—C7	119.6 (4)
N1—C5—C4	121.2 (4)	C9—C8—H8	120.2
C4—C5—C6	121.4 (4)	C7—C8—H8	120.2
N3—C15—C16	117.8 (3)	C17—C18—H18	119.6
N3—C15—C14	120.5 (4)	C19—C18—C17	120.7 (5)
C14—C15—C16	121.6 (4)	C19—C18—H18	119.6
C17—C16—C15	121.1 (4)	C1—C2—H2	120.1
C21—C16—C15	121.4 (4)	C3—C2—C1	119.8 (5)
C21—C16—C17	117.6 (4)	C3—C2—H2	120.1
N2—C10—C11	117.4 (3)	C20—C19—C18	120.0 (5)
N2—C10—C9	120.8 (4)	C20—C19—H19	120.0
C9—C10—C11	121.8 (4)	C18—C19—H19	120.0
N3—C11—C10	117.6 (3)	C14—C13—C12	119.8 (4)
N3—C11—C12	120.9 (4)	C14—C13—H13	120.1
C12—C11—C10	121.4 (4)	C12—C13—H13	120.1
N2—C6—C5	118.2 (3)	F1—C22—S1	110.9 (6)
N2—C6—C7	122.1 (4)	F1—C22—F2	109.0 (10)
C7—C6—C5	119.6 (4)	F3—C22—S1	113.8 (8)
C5—C4—H4	120.0	F3—C22—F1	111.6 (8)
C3—C4—C5	120.0 (5)	F3—C22—F2	107.2 (9)
C3—C4—H4	120.0	F2—C22—S1	103.9 (6)
N1—C1—H1	119.1		
Ag1 ⁱ —N2—C10—C11	−13.4 (4)	C15—C16—C21—C20	−177.2 (4)
Ag1 ⁱ —N2—C10—C9	164.6 (3)	C15—C14—C13—C12	−0.9 (8)
Ag1 ⁱ —N2—C6—C5	15.1 (5)	C16—C15—C14—C13	−178.0 (4)
Ag1 ⁱ —N2—C6—C7	−163.3 (3)	C16—C17—C18—C19	−2.2 (8)
Ag1 ⁱ —N3—C15—C16	7.7 (5)	C16—C21—C20—C19	−1.6 (7)
Ag1 ⁱ —N3—C15—C14	−174.5 (3)	C10—N2—C6—C5	179.7 (3)
Ag1 ⁱ —N3—C11—C10	−11.5 (4)	C10—N2—C6—C7	1.3 (6)
Ag1 ⁱ —N3—C11—C12	171.5 (3)	C10—C11—C12—C13	−174.3 (4)
Ag1—N1—C5—C6	−4.0 (5)	C10—C9—C8—C7	0.1 (7)
Ag1—N1—C5—C4	175.2 (3)	O3—S1—O1—Ag1	18.4 (9)
Ag1—N1—C1—C2	−176.2 (4)	O3—S1—C22—F1	−64.9 (9)
O2—S1—O1—Ag1	156.1 (7)	O3—S1—C22—F3	61.9 (9)
O2—S1—C22—F1	175.0 (7)	O3—S1—C22—F2	178.1 (6)
O2—S1—C22—F3	−58.2 (9)	C11—N3—C15—C16	178.0 (3)
O2—S1—C22—F2	58.0 (7)	C11—N3—C15—C14	−4.1 (6)
N2—C10—C11—N3	17.0 (5)	C11—C10—C9—C8	178.7 (4)
N2—C10—C11—C12	−166.0 (4)	C11—C12—C13—C14	−2.4 (7)
N2—C10—C9—C8	0.8 (6)	C6—N2—C10—C11	−179.5 (3)
N2—C6—C7—C8	−0.4 (6)	C6—N2—C10—C9	−1.4 (5)
N3—C15—C16—C17	−141.8 (4)	C6—C5—C4—C3	179.5 (5)
N3—C15—C16—C21	37.5 (6)	C6—C7—C8—C9	−0.3 (7)
N3—C15—C14—C13	4.2 (7)	C4—C5—C6—N2	−134.9 (4)
N3—C11—C12—C13	2.6 (6)	C4—C5—C6—C7	43.6 (6)
N1—C5—C6—N2	44.3 (5)	C4—C3—C2—C1	−1.6 (9)

N1—C5—C6—C7	−137.2 (4)	C1—N1—C5—C6	180.0 (4)
N1—C5—C4—C3	0.4 (8)	C1—N1—C5—C4	−0.8 (7)
N1—C1—C2—C3	1.2 (9)	C9—C10—C11—N3	−161.0 (3)
O1—S1—C22—F1	53.7 (9)	C9—C10—C11—C12	16.0 (6)
O1—S1—C22—F3	−179.5 (8)	C14—C15—C16—C17	40.4 (6)
O1—S1—C22—F2	−63.2 (6)	C14—C15—C16—C21	−140.3 (4)
C5—N1—C1—C2	0.1 (7)	C17—C16—C21—C20	2.1 (6)
C5—C6—C7—C8	−178.8 (4)	C17—C18—C19—C20	2.8 (9)
C5—C4—C3—C2	0.9 (9)	C21—C16—C17—C18	−0.2 (7)
C15—N3—C11—C10	177.7 (3)	C21—C20—C19—C18	−0.9 (8)
C15—N3—C11—C12	0.7 (6)	C22—S1—O1—Ag1	−90.8 (8)
C15—C16—C17—C18	179.1 (4)		

Symmetry code: (i) $-x+1, y, -z+3/2$.

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C3—H3 $\cdots$ O2 ⁱⁱ	0.93	2.43	3.273 (6)	150
C9—H9 $\cdots$ O2 ⁱⁱⁱ	0.93	2.58	3.278 (5)	132
C9—H9 $\cdots$ O1 ⁱⁱⁱ	0.93	2.65	3.315 (5)	130

Symmetry codes: (ii) $x, -y, z+1/2$; (iii) $x, -y+1, z+1/2$.