Crystal structure of tetrakis(µ-4-benzyl-4H-1,2,4-triazole-κ²N¹:N²)tetrafluoridodi-µ₂-oxido-dioxido-disilver(I)divanadium(V)

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The crystal structure of the title compound, [Ag₂(VO₂F₂)₂(C₉H₈N₃)₄], is presented. The molecular complex is based on the heterobimetallic Ag I—V V fragment [Ag₂(VVO₂F₂)₂(tr)₄] supported by four 1,2,4-triazole ligands [4-benzyl-(4H-1,2,4-triazol-4-yl)]. The triazole functional group demonstrates homo- and heterometallic connectivity (Ag—Ag and Ag—V) of the metal centers through the [–NN–] double and single bridges, respectively. The vanadium atom possesses a distorted trigonal–bipyramidal coordination environment [VO₂F₂N] with the Reedijk structural parameter τ = 0.59. In the crystal, C—H⋅⋅⋅O and C—H⋅⋅⋅F hydrogen bonds as well as C—H⋅⋅⋅π contacts are observed involving the organic ligands and the vanadium oxofluoride anions. A Hirshfeld surface analysis of the hydrogen-bonding interactions is also described.

1. Chemical context

There is considerable interest in the chemistry of organic–inorganic hybrids, including the vanadium oxide–fluoride (VOF) matrix, which is motivated by the numerous potential applications in catalysis, magnetism, optics, etc. (Dolbecq et al., 2010; Monakhov et al., 2015). Incorporation of silver(I) in VOF solid can afford materials such as Ag₄V₂O₆F₂ (Sorensen et al., 2005; Albrecht et al., 2009) and Ag₅VO₅F₄ (Chamberlain et al., 2010), which are attractive candidates for solid-state battery technologies. The formation of Ag I–VOF heterobimetallic secondary building units (SBUs) in coordination compounds remains a non-trivial challenge. The 1,2,4-triazole heterocycle, as a functional group, demonstrates a favorable coordination affinity towards AgI cations, connecting them into polynuclear units (Aromı et al., 2011). At the same time, it possesses a hidden capability to bind two different metal ions through a short –NN– bridge, usually Cu⁴–tr–MoVI (Tian et al., 2011; Lysenko et al., 2016; Senchyk et al., 2017; Zhu et al., 2012) but there are some other rare examples including Cu I–tr–MoVI (Sharga et al., 2010) and Ag I–tr–MoVI (Tian et al., 2017). This may be realized in the case of constructing SBUs with a terminal N¹-triazole function that has an open site accessible to coordination. We demonstrated this principle in the self-association of Ag I–VOF heterobimetallic coordination compounds based on [Ag₂(VVO₂F₂)₂(tr)₄] SBUs with bi-1,2,4-triazole ligands with different geometries (Senchyk et al., 2012). Such units seem to be very favorable and stable, and
form even in the presence of a heterobifunctional 1,2,4-triazole-carboxylate ligand (Senchyk et al., 2019). In the present contribution we extend the library of Ag\textsuperscript{I}–VO\textsubscript{F} compounds, adding the title complex [Ag\textsubscript{2}(VO\textsubscript{2}F\textsubscript{2})(tr-CH\textsubscript{2}Ph)]\textsubscript{4} (I), which has the ligand 4-benzyl-(4H-1,2,4-triazol-4-yl) (tr-CH\textsubscript{2}Ph).

2. Structural commentary

Compound I crystallizes in the monoclinic space group \textit{P}2\textsubscript{1}/\textit{c}. Its asymmetric unit contains one Ag\textsuperscript{I} cation, one \textit{[V}\textsubscript{2}O\textsubscript{2}F\textsubscript{4}\textit{]}\textsuperscript{+1} anion and two organic ligands (tr-CH\textsubscript{2}Ph), which, after inversion across a center of symmetry, form the molecular tetranuclear cluster [Ag\textsubscript{2}(V\textsubscript{2}O\textsubscript{2}F\textsubscript{4})(tr-CH\textsubscript{2}Ph)\textsubscript{4}] (Fig. 1). Two 1,2,4-triazole ligands bridge two adjacent silver atoms [the Ag···Ag\textsuperscript{I} distance is 4.2497 (5) Å; symmetry code (i) \(-x, -y+1, -z\)], while the other two link Ag and V centers [the Ag···V distance is 3.8044 (6) Å]. Thus, the coordination environment of the Ag\textsuperscript{I} cation can be described as [Ag\textsubscript{N,O}] with typical Ag···N(triazole) bond lengths [in the range of 2.197 (2) – 2.390 (3) Å] and elongated Ag···O bond [2.562 (2) Å] (Table 1). The V\textsuperscript{V} atom possesses a distorted trigonal–bipyramidal coordination environment [VO\textsubscript{2}F\textsubscript{2}N] with V···F [1.632 (2) and 1.660 (2) Å] and elongated V···O [2.203 (2) Å] bonds (Table 1). The geometry of the vanadium oxofluoride polyhedra is characterized by the Reedijk structural parameter \(\tau\) (Addison et al., 1984) of 0.59 (for a square-pyramidal geometry, \(\tau = 0\) and for trigonal–bipyramidal, \(\tau = 1\)). A bond-valence-sum calculation for the [VO\textsubscript{2}F\textsubscript{2}N] polyhedra confirms the +5 oxidation state for the vanadium atom.

3. Supramolecular features

Since the organic ligand contains a hydrophobic benzyl tail, the crystal structure of I involves no solvate water molecules. Thus, the only hydrogen bonds observed are of the type C···H···O, C···H···F and C···H···π contacts (Figs. 2 and 3, Table 2). The central 1,2,4-triazole unit, which bridges two Ag ions, displays intramolecular C10···H10···O2 [3.082 (4) Å] and intermolecular C11···H11···F1\textsuperscript{v} [2.935 (4) Å, symmetry code (v) \(-x+1, -y+1, -z\)] hydrogen-bond contacts.

![Figure 1](image1.png)

Figure 1
The molecular structure of compound I, showing the atom-labeling scheme [symmetry code: (i) \(-x, -y+1, -z\)]. Displacement ellipsoids are drawn at the 30% probability level.
other triazole group, which provides the heterometallic Ag–V linkage, forms bifurcated C—H/O and C—H/F contacts with vanadium oxofluoride anions of neighboring molecular complexes. Additionally, methylene –CH2– fragments show directed C—H/O and C—H/F contacts to the VOF fragments. The phenyl rings are here oriented towards each other in an edge-to-face C—H/π interaction mode.

Supramolecular interactions in the title structure were studied through Hirshfeld surface analysis (Spackman & Byrom, 1997; McKinnon et al., 2004; Hirshfeld, 1977; Spackman & McKinnon, 2002), performed with CrystalExplorer17 (Turner et al., 2017), taking into account only the major contribution of the disordered group. The Hirshfeld surface, mapped over $d_{\text{norm}}$ using a fixed color scale of $-0.488$ (red) to $1.385$ (blue) a.u. visualizes the set of shortest intermolecular contacts (Fig. 4). All of them correspond to the hydrogen-bond interactions, which fall into three categories. The strongest hydrogen bonds to F-atom acceptors are reflected by the most prominent red spots ($-0.469$ to $-0.488$ a.u.), whereas a group of medium intensity spots ($-0.182$ to $-0.261$ a.u.) identify weaker C—H/O bonds with the terminal oxide O2. However, even more distal interactions with the bridging oxide O1 are still distinguishable on the surface, in the form of very diffuse, less intense spots ($-0.066$ to $-0.142$ a.u.).

The contribution of different kinds of interatomic contacts to the Hirshfeld surface is shown in the fingerprint plots in Fig. 5. A significant fraction of the E····-H/H····E (E = C, N, O, F) contacts (in total 60.1%) suggests the dominant role of the hydrogen-bond interactions. The strongest ones (E = O, F) have a similar nature and they are reflected by pairs of spikes pointing to the lower left of the plot. However, the contribution from the contacts with F-atom acceptors is higher (15.6% for F····-H/H····F and 11.6% for O····-H/H····O) and they are also essentially shorter, as indicated by different lengths of the spikes (the shortest contacts are F····-H = 2.0 and O····-H = 2.2 Å). One may suppose that the preferable sites for hydrogen bonding of the vanadium oxofluoride groups are the F-atoms. This is consistent with the results of Hirshfeld analysis for the $[\text{VOF}_3]^2-$ anion 4,4'-(propane-1,3-diyl)bis(4H-1,2,4-triazol-1-ium) salt (Senchyk et al., 2020).

The plots indicate close resemblance of the N····-H/H····C (10.7%) and C····-H/H····C (22.2%) contacts, which appear as pairs of nearly identical, very diffuse and short features

![Figure 2](image2.png)

Projection on the bc plane showing the crystal packing of compound I. Vanadium oxofluoride anions are shown as polyhedra. [Atoms are colored as follows: silver – cyan, vanadium – dark green, oxygen – red, fluorine – green, nitrogen – blue, carbon – gray; hydrogen – white.]

![Figure 3](image3.png)

Hydrogen-bonding arrangement in the structure of I showing C—H····O and C—H····F contacts [symmetry codes: (ii) $x-1$, $y$, $z$; (iii) $-x$, $-y+1$, $-z+1$; (iv) $-x+1$, $-y+1$, $-z+1$; (v) $-x+1$, $-y+1$, $-z$; (vi) $x$, $-y+1$, $z-\frac{1}{2}$]. Phenyl groups are omitted for clarity.

![Figure 4](image4.png)

The Hirshfeld surface of the title compound mapped over $d_{\text{norm}}$ in the color range $-0.488$ (red) to $1.385$ (blue) a.u., in the environment of the closest neighbor [symmetry code: $-x+1$, $-y+1$, $-z$], with the red spots indicating different kinds of intermolecular interactions.
(N⋯H = 2.9 and C⋯H = 2.9 Å). Both of them correspond to edge-to-face stacking or C–H⋯π interactions involving either the phenyl or triazole rings. The contribution from mutual π–π interactions of the latter delivers minor fractions of the C⋯C, N⋯N and C⋯N/N⋯C contacts, which account in total for only 2.6%. The shortest contact of this series [C⋯N = 3.5 Å] exceeds the sum of the van der Waals radii [3.25 Å] and π–π interactions are not associated with red spots of the dnorm surface. A comparable contribution is due to the distal anagostic contacts Ag⋯H/⋯H⋯Ag (2.9%) with the polarized methylene H atoms. There are no mutual π–π interactions involving phenyl rings, which are responsible for larger fractions of the C⋯C contacts in the case of polycyclic species (Spackman & McKinnon, 2002).

4. Database survey

A structure survey was carried out in the Cambridge Structural Database (CSD version 5.43, update of November 2021; Groom et al., 2016) for 4-benzyl-(4H-1,2,4-triazol-4-yl) and it revealed five hits for coordination compounds based on this ligand. There are no examples of AgIII compounds, only two FeII complexes [FAYQAA (Pittala et al., 2017a) and XASVEV (Pittala et al., 2017b)] and three CuII–POM complexes [YUGLIX and YUGLOD (Tian et al., 2015) and ZUXLAI (Zhang et al., 2020)]. Moreover, there are no examples of heterometallic connection through an –NN–triazole bridge for the 4-benzyl-(4H-1,2,4-triazol-4-yl) ligand.

5. Synthesis and crystallization

4-Benzyl-(4H-1,2,4-triazol-4-yl) (tr-CH2Ph) was synthesized by refluxing benzylamine (5.35 g, 50.0 mmol) and dimethylformamide azine (17.75 g, 125.0 mmol) in the presence of toluenesulfonic acid monohydrate (0.86 g, 5.0 mmol) as a catalyst in DMF (30.0 ml).

Compound I was prepared under hydrothermal conditions. A mixture of AgOAc (16.7 mg, 0.100 mmol), tr-CH2Ph (20.7 mg, 0.130 mmol), V2O5 (9.1 mg, 0.050 mmol) and 5 mL of water with aqueous HF (17.5 g, 125.0 mmol) was added into a Teflon vessel. Then the components were heated at 423 K for 24 h and slowly cooled to room temperature over 50 h, yielding light-yellow prisms of I (yield 33.4 mg, 61%).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. For one of the organic ligands, the benzyl linkage (C12–C18) is unequally disordered over two overlapping positions with refined partial contribution factors of 0.68 (3) and 0.32 (3). The major part of the disorder was freely refined anisotropically, while atoms of the minor contributor were refined anisotropically with a restrained geometry for the phenyl ring, rigid-bond restraints applied to the –CH2C6H5 linkage and similarity restraints applied to the closely separated contributions of C12 and C12A, C13 and C13A. H atoms were positioned geometrically and refined as

| Table 3: Experimental details. |
|--------------------------------|
| Crystal data                  |
| Chemical formula              | [Ag2V2F4O4(C9H9N3)4]       |
| M, g/mol                     | 1094.39                    |
| Crystal system, space group  | Monoclinic, P2_1/c         |
| Temperature (K)              | 296                        |
| a, b, c (Å)                  | 7.5484 (2), 21.2439 (6), 12.5910 (4) |
| β (°)                        | 90.910 (2)                 |
| V (Å³)                       | 2018.81 (10)               |
| Z                             | 2                         |
| Radiation type               | Mo Kα                      |
| μ (mm⁻¹)                     | 1.48                       |
| Crystal size (mm)            | 0.27 × 0.14 × 0.12         |
| Data collection              | Bruker APEXII area-detector |
| Absorption correction        | multi-scan (SADABS; Bruker, 2008) |
| Tmin, Tmax                   | 0.657, 0.856               |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 22923, 5125, 3468 |
| Rint                         | 0.044                      |
| (sin θ/λ)max (Å⁻¹)           | 0.676                      |
| Refinement                    |                            |
| R(R=2 > 2σ(F²), w(R(F²)), S | 0.038, 0.078, 1.02         |
| No. of reflections            | 5125                       |
| No. of parameters             | 323                        |
| No. of restraints             | 65                         |
| H-atom treatment             | H-atom parameters constrained |
| Δρmax                         | 0.58, –0.42                |

Figure 5: Two-dimensional fingerprint plots for the title compound, and those delineated into the principal contributions of H–H, C–H–π–π, F–H–H/⋯F, O–H–O–⋯N, N–H–H–⋯N, C–H–C, C–N/N⋯C and Ag⋯H–H/⋯Ag contacts. Other observed contacts are N⋯N (0.4%), C⋯F/⋯C (0.1%) and C⋯O/⋯O/⋯C (0.1%).
riding, with C—H = 0.93 Å (CH) and 0.97 Å (CH₂) and with 
$U_{iso}(H) = 1.2U_{eq}(C)$.

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Crystal structure of tetrakis(μ-4-benzyl-4H-1,2,4-triazole-κ²N¹:N²)tetrafluoridodi-μ₂-oxido-dioxidodisilver(I)divanadium(V)

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Computing details
Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT (Bruker, 2008); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL2014/7 (Sheldrick, 2015); molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: WinGX (Farrugia, 2012).

Tetrakis(μ-4-benzyl-4H-1,2,4-triazole-κ²N¹:N²)tetrafluoridodi-μ₂-oxido-dioxidodisilver(I)divanadium(V)

Crystal data
[Ag₂V₂F₄O₄(C₉H₉N₃)₄]
Mr = 1094.39
Monoclinic, P2₁/c
a = 7.5484 (2) Å
b = 21.2439 (6) Å
c = 12.5910 (4) Å
β = 90.910 (2)°
V = 2018.81 (10) Å³
Z = 2

F(000) = 1088
Dₐ = 1.800 Mg m⁻³
Mo Kα radiation, λ = 0.71073 Å
Cell parameters from 4931 reflections
θ = 2.5–23.8°
µ = 1.48 mm⁻¹
T = 296 K
Block, colorless
0.27 × 0.14 × 0.12 mm

Data collection
Bruker APEXII area-detector diffractometer
Radiation source: fine-focus sealed tube
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2008)
Tmin = 0.657, Tmax = 0.856
5125 independent reflections
3468 reflections with I > 2σ(I)
Rint = 0.044
θmax = 28.7°, θmin = 1.9°
h = −10→10
k = −26→28
l = −16→14
22923 measured reflections

Refinement
Refinement on F²
Least-squares matrix: full
R[F² > 2σ(F²)] = 0.038
wR(F²) = 0.078
S = 1.02
5125 reflections
323 parameters
65 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
w = 1/[σ²(Fo²) + (0.0194P)² + 2.1764P]
where P = (Fo² + 2Fc²)/3
(Δ/σ)max = 0.001
Δρmax = 0.58 e Å⁻³
Δρmin = −0.42 e Å⁻³

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**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)**

| Atom | x       | y       | z       | Uiso/Usq | Occ. (<1) |
|------|---------|---------|---------|----------|-----------|
| Ag1  | 0.00892 (3) | 0.49751 (2) | 0.16871 (2) | 0.04174 (9) |           |
| V1   | 0.43103 (7)  | 0.48341 (2) | 0.33615 (4)  | 0.03165 (13) |           |
| F1   | 0.6173 (3)   | 0.42871 (13) | 0.32820 (16) | 0.0802 (8)   |           |
| F2   | 0.3957 (2)   | 0.45217 (9)  | 0.46985 (15) | 0.0471 (5)   |           |
| O1   | 0.3065 (3)   | 0.45593 (10) | 0.23966 (17) | 0.0407 (5)   |           |
| O2   | 0.5296 (3)   | 0.54823 (11) | 0.29314 (16) | 0.0424 (6)   |           |
| N1   | 0.0417 (3)   | 0.54163 (12) | 0.32878 (19) | 0.0315 (6)   |           |
| N2   | 0.2025 (3)   | 0.54132 (11) | 0.38181 (19) | 0.0301 (6)   |           |
| N3   | 0.0147 (3)   | 0.59315 (11) | 0.47783 (18) | 0.0292 (6)   |           |
| N4   | 0.2055 (4)   | 0.54025 (13) | 0.0405 (2)   | 0.0386 (6)   |           |
| N5   | 0.1929 (3)   | 0.54905 (12) | −0.06853 (19)| 0.0345 (6)   |           |
| N6   | 0.4464 (3)   | 0.58619 (12) | −0.0125 (2)  | 0.0342 (6)   |           |
| C1   | −0.0684 (4)  | 0.57241 (14) | 0.3893 (2)   | 0.0337 (7)   |           |
| H1   | −0.1876     | 0.5790    | 0.3732     | 0.040*      |           |
| C2   | 0.1821 (4)   | 0.57219 (14) | 0.4702 (2)  | 0.0328 (7)   |           |
| H2   | 0.2710      | 0.5788    | 0.5209     | 0.039*      |           |
| C3   | −0.0650 (4)  | 0.62351 (15) | 0.5708 (2)  | 0.0400 (8)   |           |
| H3A  | −0.0579     | 0.5945    | 0.6301     | 0.048*      |           |
| H3B  | −0.1896     | 0.6308    | 0.5552     | 0.048*      |           |
| C4   | 0.0174 (4)   | 0.68457 (14) | 0.6044 (2)  | 0.0308 (7)   |           |
| C5   | 0.0024 (5)   | 0.73774 (17) | 0.5430 (3)  | 0.0490 (9)   |           |
| H5   | −0.0493     | 0.7354    | 0.4756     | 0.059*      |           |
| C6   | 0.0646 (6)   | 0.79525 (19) | 0.5816 (4)  | 0.0696 (13)  |           |
| H6   | 0.0537      | 0.8314    | 0.5403     | 0.084*      |           |
| C7   | 0.1417 (6)   | 0.7982 (2)  | 0.6806 (5)  | 0.0775 (15)  |           |
| H7   | 0.1817      | 0.8367    | 0.7068     | 0.093*      |           |
| C8   | 0.1607 (6)   | 0.7456 (3)  | 0.7410 (4)  | 0.0752 (14)  |           |
| H8   | 0.2152      | 0.7479    | 0.8076     | 0.090*      |           |
| C9   | 0.0986 (5)   | 0.68877 (19) | 0.7030 (3)  | 0.0517 (10)  |           |
| H9   | 0.1118      | 0.6528    | 0.7444     | 0.062*      |           |
| C10  | 0.3594 (4)   | 0.56283 (15) | 0.0704 (2)  | 0.0385 (8)   |           |
| H10  | 0.4025      | 0.5627    | 0.1400     | 0.046*      |           |
| C11  | 0.3391 (4)   | 0.57667 (15) | −0.0972 (2) | 0.0369 (7)   |           |
| H11  | 0.3652      | 0.5881    | −0.1665    | 0.044*      |           |
| C12  | 0.6224 (7)   | 0.6171 (4)  | −0.0050 (16)| 0.040 (3)    | 0.68 (3)   |
| H12A | 0.7076      | 0.5936    | −0.0462    | 0.048*      | 0.68 (3)   |
| H12B | 0.6633      | 0.6178    | 0.0684     | 0.048*      | 0.68 (3)   |
| C13  | 0.608 (2)    | 0.6830 (4)  | −0.0465 (10)| 0.0356 (18)  | 0.68 (3)   |
| C14  | 0.5342 (18)  | 0.7259 (6)  | 0.0216 (12) | 0.049 (2)    | 0.68 (3)   |

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### Atomic Displacement Parameters (Å²)

|       | U₁¹  | U₂²  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|-------|------|------|------|------|------|------|
| Ag1   | 0.04650 (15) | 0.04865 (17) | 0.02972 (13) | 0.00637 (12) | 0.01010 (10) | 0.00375 (12) |
| V1    | 0.0375 (3) | 0.0324 (3) | 0.0249 (3) | 0.0025 (2) | 0.0031 (2) | 0.0009 (2) |
| F1    | 0.0848 (17) | 0.121 (2) | 0.0337 (12) | 0.0688 (16) | 0.0171 (12) | 0.0150 (13) |
| F2    | 0.0453 (11) | 0.0559 (13) | 0.0398 (11) | 0.0063 (9) | 0.0038 (9) | 0.0181 (9) |
| O1    | 0.0490 (14) | 0.0397 (13) | 0.0330 (12) | 0.0045 (10) | 0.0085 (11) | 0.0072 (10) |
| O2    | 0.0326 (12) | 0.0692 (16) | 0.0253 (11) | 0.0118 (11) | 0.0045 (10) | 0.0048 (11) |
| N1    | 0.0264 (13) | 0.0414 (16) | 0.0264 (13) | 0.0014 (11) | 0.0060 (11) | 0.0052 (11) |
| N2    | 0.0282 (13) | 0.0329 (14) | 0.0290 (14) | 0.0001 (11) | 0.0083 (11) | 0.0044 (11) |
| N3    | 0.0341 (14) | 0.0300 (14) | 0.0235 (14) | 0.0013 (11) | 0.0001 (11) | 0.0039 (10) |
| N4    | 0.0502 (17) | 0.0411 (16) | 0.0242 (14) | 0.0115 (13) | 0.0049 (12) | 0.0053 (12) |
| N5    | 0.0402 (15) | 0.0408 (16) | 0.0223 (13) | 0.0068 (12) | 0.0028 (12) | 0.0022 (11) |
| N6    | 0.0363 (14) | 0.0373 (15) | 0.0287 (14) | 0.0043 (11) | 0.0056 (12) | 0.0021 (11) |
| C1    | 0.0256 (16) | 0.0412 (19) | 0.0341 (17) | 0.0004 (13) | 0.0084 (14) | 0.0044 (14) |
| C2    | 0.0309 (16) | 0.0373 (18) | 0.0300 (17) | 0.0005 (13) | 0.0085 (14) | 0.0051 (14) |
| C3    | 0.047 (2)  | 0.0395 (19) | 0.0337 (18) | 0.0056 (15) | 0.0107 (16) | 0.0084 (15) |
| C4    | 0.0270 (16) | 0.0316 (17) | 0.0339 (17) | 0.0017 (13) | 0.0031 (13) | 0.0065 (13) |
| C5    | 0.046 (2)  | 0.046 (2)  | 0.055 (2)  | 0.0040 (17) | 0.0043 (18) | 0.0073 (18) |
| C6    | 0.062 (3)  | 0.037 (2)  | 0.110 (4)  | 0.004 (2)  | 0.013 (3)  | 0.009 (2)  |
| C7    | 0.070 (3)  | 0.062 (3)  | 0.101 (4)  | 0.024 (2)  | 0.023 (3)  | 0.043 (3)  |
| C8    | 0.067 (3)  | 0.105 (4)  | 0.053 (3)  | 0.028 (3)  | 0.001 (2)  | 0.034 (3)  |
| C9    | 0.054 (2)  | 0.062 (3)  | 0.039 (2)  | 0.0041 (19) | 0.0045 (18) | 0.0032 (18) |
### Geometric parameters (Å, °)

| Bond          | Length (Å) | Angle (°) | Length (Å) | Angle (°) | Length (Å) | Angle (°) |
|---------------|------------|-----------|------------|-----------|------------|-----------|
| Ag1—N5i       | 2.197 (2)  | C7—H7     | 0.9300     |           |            |           |
| Ag1—N1        | 2.233 (2)  | C8—C9     | 1.378 (6)  |           |            |           |
| Ag1—N4        | 2.390 (3)  | C8—H8     | 0.9300     |           |            |           |
| Ag1—O1        | 2.562 (2)  | C9—H9     | 0.9300     |           |            |           |
| V1—O1         | 1.632 (2)  | C10—H10   | 0.9300     |           |            |           |
| V1—O2         | 1.660 (2)  | C11—H11   | 0.9300     |           |            |           |
| V1—F1         | 1.828 (2)  | C12—C13   | 1.497 (5)  |           |            |           |
| V1—F2         | 1.8330 (18)| C12—H12A  | 0.9700     |           |            |           |
| V1—N2         | 2.203 (2)  | C12—H12B  | 0.9700     |           |            |           |
| N1—C1         | 1.311 (4)  | C13—C18   | 1.374 (9)  |           |            |           |
| N1—N2         | 1.376 (3)  | C13—C14   | 1.375 (8)  |           |            |           |
| N2—C2         | 1.303 (4)  | C14—C15   | 1.386 (11) |           |            |           |
| N3—C1         | 1.345 (4)  | C14—H14   | 0.9300     |           |            |           |
| N3—C2         | 1.345 (4)  | C15—C16   | 1.371 (12) |           |            |           |
| N3—C3         | 1.473 (4)  | C15—H15   | 0.9300     |           |            |           |
| N4—C10        | 1.306 (4)  | C16—C17   | 1.344 (13) |           |            |           |
| N4—N5         | 1.387 (3)  | C16—H16   | 0.9300     |           |            |           |
| N5—C11        | 1.306 (4)  | C17—C18   | 1.390 (11) |           |            |           |
| N5—Ag1i       | 2.197 (2)  | C17—H17   | 0.9300     |           |            |           |
| N6—C10        | 1.339 (4)  | C18—H18   | 0.9300     |           |            |           |
| N6—C11        | 1.344 (4)  | C12A—C13A | 1.497 (6)  |           |            |           |
| N6—C12A       | 1.484 (5)  | C12A—H12C | 0.9700     |           |            |           |
| N6—C12        | 1.484 (5)  | C12A—H12D | 0.9700     |           |            |           |
| C1—H1         | 0.9300     | C13A—C14A | 1.3900     |           |            |           |
| C2—H2         | 0.9300     | C13A—C18A | 1.3900     |           |            |           |
| C3—C4         | 1.497 (4)  | C14A—C15A | 1.3900     |           |            |           |
| C3—H3A        | 0.9700     | C14A—H14A | 0.9300     |           |            |           |
| C3—H3B        | 0.9700     | C15A—C16A | 1.3900     |           |            |           |
| C4—C5         | 1.372 (5)  | C15A—H15A | 0.9300     |           |            |           |
C4—C9 1.378 (4) C16A—C17A 1.390
C5—C6 1.393 (5) C16A—H16A 0.930
C5—H5 0.9300 C17A—C18A 1.390
C6—C7 1.369 (6) C17A—H17A 0.930
C6—H6 0.9300 C18A—H18A 0.930
C7—C8 1.358 (7)

N5i—Ag1—N1 140.62 (9) C7—C8—C9 119.6 (4)
N5i—Ag1—N4 102.45 (9) C7—C8—H8 120.2
N1—Ag1—N4 112.90 (9) C9—C8—H9 120.2
N5i—Ag1—O1 129.87 (8) C8—C9—H9 120.2
N1—Ag1—O1 75.28 (8) C4—C9—H9 120.2
N4—Ag1—O1 79.39 (8) C4—C9—H9 120.2
O1—V1—O2 108.04 (11) N4—C10—N6 110.8 (3)
O1—V1—F1 99.57 (11) N4—C10—H10 124.6
O2—V1—F1 99.21 (13) N6—C10—H10 124.6
O1—V1—F2 117.63 (10) N5—C11—N6 110.5 (3)
O2—V1—F2 132.25 (10) N5—C11—H11 124.8
F1—V1—F2 86.76 (10) N6—C11—H11 124.8
O1—V1—N2 87.14 (10) N6—C12—C13 109.3 (8)
O2—V1—N2 88.78 (11) N6—C12—H12 109.8
F1—V1—N2 167.32 (10) C13—C12—H12 109.8
F2—V1—N2 80.59 (9) N6—C12—H12 109.8
V1—O1—Ag1 128.89 (11) C13—C12—H12B 109.8
C1—N1—N2 106.4 (2) C17—C16—C15 118.9 (7)
C1—N1—Ag1 132.19 (19) C18—C13—C14 125.6 (13)
N2—N1—Ag1 121.35 (18) N6—C12—H12 115.5 (13)
C2—N2—N1 107.3 (2) C14—C13—C14 120.4 (8)
C2—N2—V1 127.4 (2) C13—C14—H14 119.8
N1—N2—V1 124.36 (18) C16—C15—C14 119.2 (9)
C1—N3—C2 105.0 (2) C16—C15—H15 120.4
C1—N3—C3 127.7 (3) C16—C15—H15 120.4
C2—N3—C3 126.7 (3) C16—C15—H15 120.4
C10—N4—N5 106.5 (2) C14—C15—H15 120.4
C10—N4—Ag1 120.2 (2) C17—C16—C15 121.4 (8)
N5—N4—Ag1 133.30 (19) C17—C16—H16 119.3
C11—N5—N4 106.8 (2) C15—C16—H16 119.3
C11—N5—Ag1i 128.7 (2) C16—C17—C18 119.4 (8)
N4—N5—Ag1i 122.94 (19) C16—C17—H17 120.3
C10—N6—C11 105.4 (3) C18—C17—H17 120.3
C10—N6—C12A 134.8 (15) C13—C18—C17 120.7 (9)
C11—N6—C12A 119.7 (15) C13—C18—H18 119.7
C10—N6—C12 124.3 (8) C17—C18—H18 119.7
C11—N6—C12 130.2 (7) N6—C12A—C13A 113.8 (16)
N1—C1—N3 110.7 (3) N6—C12A—H12C 108.8
N1—C1—H1 124.6 C13A—C12A—H12C 108.8
N3—C1—H1 124.6 N6—C12A—H12D 108.8
N2—C2—N3 110.6 (3) C13A—C12A—H12D 108.8
N2—C2—H2 124.7 H12C—C12A—H12D 107.7
N3—C2—H2 124.7 C14A—C13A—C18A 120.0
N3—C3—C4 115.5 (3) C14A—C13A—C12A 131.1 (18)
N3—C3—H3A 108.4 C18A—C13A—C12A 108.9 (19)
C4—C3—H3A 108.4 C13A—C14A—C15A 120.0
N3—C3—H3B 108.4 C13A—C14A—H14A 120.0
C4—C3—H3B 108.4 C15A—C14A—H14A 120.0
H3A—C3—H3B 107.5 C16A—C15A—C14A 120.0
C5—C4—C9 119.0 (3) C16A—C15A—H15A 120.0
C5—C4—C3 121.6 (3) C14A—C15A—H15A 120.0
C9—C4—C3 119.2 (3) C15A—C16A—C17A 120.0
C4—C5—C6 120.1 (4) C15A—C16A—H16A 120.0
C4—C5—H5 120.0 C17A—C16A—H16A 120.0
C6—C5—H5 120.0 C18A—C17A—C16A 120.0
C7—C6—C5 119.6 (4) C18A—C17A—H17A 120.0
C7—C6—H6 120.2 C16A—C17A—H17A 120.0
C5—C6—H6 120.2 C17A—C18A—C13A 120.0
C8—C7—C6 120.8 (4) C17A—C18A—H18A 120.0
C8—C7—H7 119.6 C13A—C18A—H18A 120.0
C6—C7—H7 119.6

O2—V1—O1—Ag1 −74.41 (17) Ag1—N4—C10—N6 −178.0 (2)
F1—V1—O1—Ag1 −177.46 (15) C11—N6—C10—N4 −0.4 (4)
F2—V1—O1—Ag1 91.19 (15) C12A—N6—C10—N4 178.8 (12)
N2—V1—O1—Ag1 13.37 (14) C12—N6—C10—N4 178.0 (6)
C1—N1—N2—Ag1 168.9 (2) C10—N6—C11—N5 0.2 (4)
N1—N2—C2—N3 −12.7 (3) C12A—N6—C11—N5 −179.2 (10)
C10—N4—N5—C11 177.9 (2) C12—N6—C11—N5 −178.1 (7)
C11—N4—N5—Ag1 166.2 (2) C10—N6—C12—C13 57.3 (15)
C10—N4—N5—Ag1 15.5 (4) C11—N6—C12—C13 −101.7 (13)
N1—N2—C2—N3 1.3 (3) C12—N6—C11—N5 77.8 (15)
Ag1—N1—C1—N3 −176.8 (2) C12—C13—C14—C15 0.4 (10)
C2—N3—C1—N1 1.4 (3) C12—C13—C14—C15 −179.1 (13)
C3—N3—C1—N1 −172.8 (3) C13—C14—C15—C16 0.1 (13)
N1—N2—C2—N3 −0.2 (3) C14—C15—C16—C17 −1.3 (15)
V1—N2—C2—N3 −169.37 (19) C15—C16—C17—C18 1.8 (15)
C1—N3—C2—N2 1.0 (3) C14—C13—C18—C17 0.0 (10)
C3—N3—C2—N2 172.5 (3) C12—C13—C18—C17 179.5 (15)
C1—N3—C3—C4 −128.2 (3) C16—C17—C18—C13 −1.1 (13)
C2—N3—C3—C4 62.2 (4) C10—N6—C12A—C13A −113 (2)
N3—C3—C4—C5 68.5 (4) C11—N6—C12A—C13A 66 (3)
N3—C3—C4—C9 −116.6 (3) N6—C12A—C13A—C14A 62 (4)
C9—C4—C5—C6 −1.7 (5) N6—C12A—C13A—C18A −117 (2)
C3—C4—C5—C6 173.3 (3) C18A—C13A—C14A—C15A 0.0
C4—C5—C6—C7 0.5 (6) C12A—C13A—C14A—C15A −179 (3)
| Bond                  | Angle (°) | Symmetry Code |
|----------------------|-----------|---------------|
| C5—C6—C7—C8         | 0.9 (7)   |               |
| C6—C7—C8—C9         | −1.1 (7)  |               |
| C7—C8—C9—C4         | −0.1 (7)  |               |
| C5—C4—C9—C8         | 1.5 (5)   |               |
| C3—C4—C9—C8         | −173.6 (4)|               |
| N5—N4—C10—N6        | 0.5 (4)   |               |

Symmetry code: (i) −x, −y+1, −z.

### Hydrogen-bond geometry (Å, °)

| D—H···A                  | D—H | H···A | D···A | D—H···A |
|--------------------------|------|-------|-------|---------|
| C1—H1···O2···           | 0.93 | 2.44  | 3.289 (4) | 153     |
| C1—H1···F2···           | 0.93 | 2.63  | 3.108 (4) | 113     |
| C2—H2···F1···           | 0.93 | 2.07  | 2.935 (4) | 154     |
| C2—H2···F2···           | 0.93 | 2.60  | 3.304 (4) | 133     |
| C3—H3···O1···           | 0.97 | 2.73  | 3.465 (4) | 133     |
| C3—H3···O2···           | 0.97 | 2.37  | 3.006 (4) | 123     |
| C10—H10···O2···         | 0.93 | 2.16  | 3.082 (4) | 170     |
| C11—H11···F1···         | 0.93 | 2.07  | 2.935 (4) | 153     |
| C12—H12···O1···         | 0.97 | 2.65  | 3.388 (2)  | 133     |
| C16—H16···O2···         | 0.93 | 2.42  | 3.339 (9)  | 172     |
| C18—H18···O1···         | 0.93 | 2.83  | 3.589 (15) | 139     |

Symmetry codes: (ii) x−1, y, z; (iii) −x, −y+1, −z+1; (iv) −x+1, −y+1, −z+1; (v) −x+1, −y+1, −z; (vi) x, −y+3/2, z−1/2.