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Bis[μ-4′-(2-pyridyl)-2,2′:6′,2″-terpyridine]disilver(I) bis(hexafluorophosphate)

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The Ag atoms and the ligands of the dication in the title compound, $[Ag_2(C_{20}H_{14}N_4)_2](PF_6)_2$, are disordered; the dication lies on a center of symmetry. The major component is chelated by two N atoms of the heterocycle and is coordinated by the N atom of the pyridyl substituent of the other heterocycle; the geometry is trigonal planar distorted towards tetrahedral owing to a weak Ag$\cdots$F interaction. The minor component is chelated by three N atoms and is also coordinated by the N atom of the pyridyl substituent of the inversion-related heterocycle; its geometry is octahedral owing to two Ag$\cdots$F interactions. One anion lies on a special position of site symmetry 2 and the other on a special position of site symmetry $\overline{1}$. The disorder in the centrosymmetric dication is best described in terms of the Ag atom being disordered over two sites and the C_5H_2N ring of the heterocycle being rotated by about 180°; the two dications are superimposed in the crystal structure.

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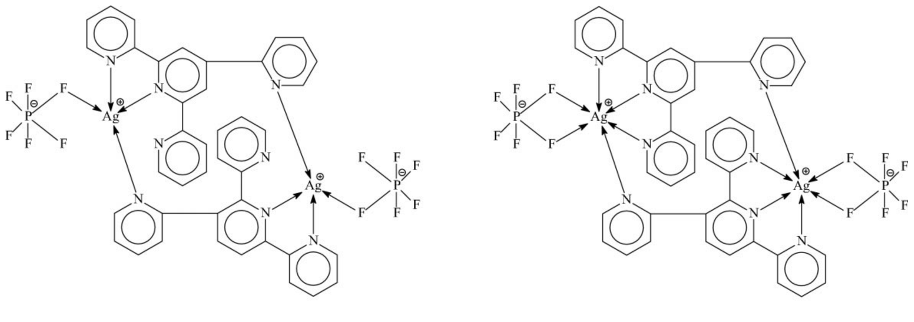
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
R factor = 0.068
wR factor = 0.203
Data-to-parameter ratio = 15.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Along with other studies on the metal complexes of substituted 2,2′:6′,2″-terpyridines (Andres & Schubert, 2004; Heller & Schubert, 2003), we have used the terdentate 4′-aryl-2,2′:6′,2″-terpyridine N-heterocycles to bind to metal(I) ions (Hou, Li, Wu, *et al.*, 2004; Hou, Li, Yin *et al.*, 2004; Hou & Li, 2005). The present study has, as the aryl substituent, a pyridyl group, which is expected to interact with a neighboring metal to give rise to a dinuclear or oligonuclear complex. This is realised here in the silver hexafluorophosphate salt, which exists as a dinuclear complex, (I).



Major disorder component

Minor disorder component

(I)

The Ag atom of the $[(C_{20}H_{14}N_4)_2Ag_2]^{2+}$ dication is disordered over two sites such that the major component is chelated by only two N atoms of one heterocycle through its terpyridyl portion. The pyridyl substituent of the symmetry-related heterocycle coordinates to this Ag atom, whose

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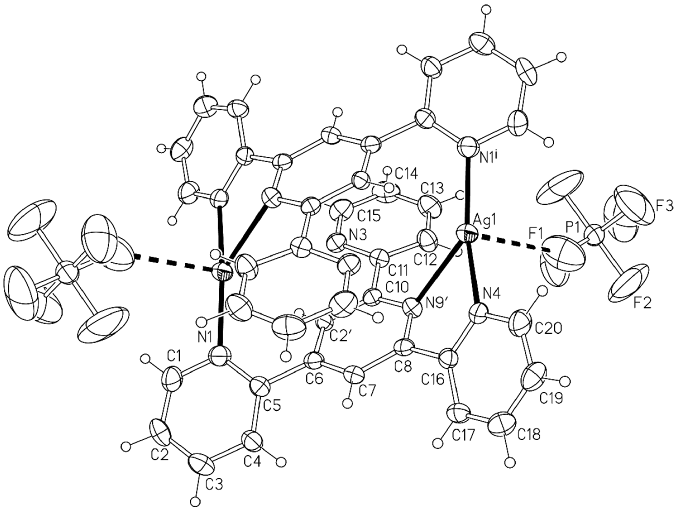

Figure 1
ORTEPII plot (Johnson, 1976) of (I), showing the major Ag1 disordered atom. The anion lies on a special position of site symmetry 2. Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as spheres of arbitrary radii.

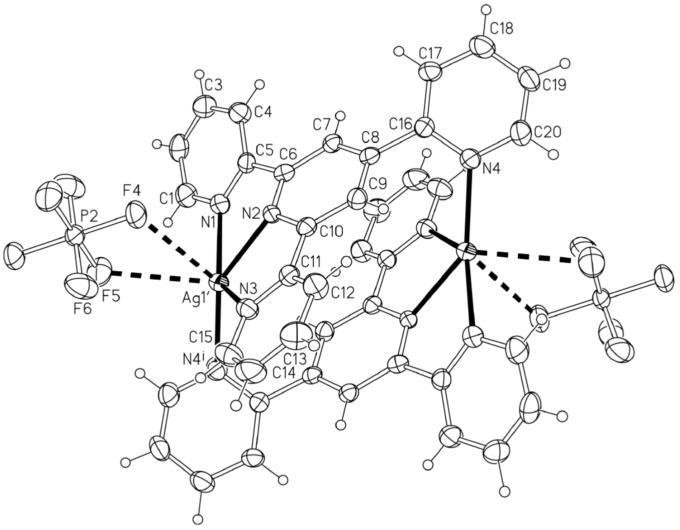

Figure 2
ORTEPII plot (Johnson, 1976) of (I), showing the minor Ag1′ disordered atom. The anion lies on a special position of site symmetry $\bar{1}$. Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as spheres of arbitrary radii.

geometry is better regarded as tetrahedral, arising from an Ag$\cdots$F interaction (Fig. 1). On the other hand, the minor Ag atom is chelated by three N atoms of the terpyridyl portion, and it is also coordinated by the pyridyl substituent of the other heterocycle. Two Ag$\cdots$F interactions confer an octahedral coordination environment on the atom (Fig. 2). The scheme depicts the formula unit of the the major and minor components. One anion lies on a special position of site symmetry 2 and the other on a special position of site symmetry $\bar{1}$.

The disorder in the centrosymmetric dication is best described in terms of the Ag atom being disordered over two sites and the C_5H_2N ring of the heterocycle being rotated by about 180°; the two dications are superimposed in the crystal structure.

Experimental

4′-(2-Pyridyl)-2,2′:6′,2″-terpyridine was synthesized using a modification of a literature method (Constable & Thompson, 1992). An acetone solution (10 ml) of the ligand (0.155 g, 0.5 mmol) was added to an ethanol solution (5 ml) of silver hexafluorophosphate (0.126 g, 0.5 mmol). The clear solution was set aside for a few days, after which block-shaped crystals separated in about 70% yield. Analysis calculated for $C_{40}H_{28}Ag_2F_{12}N_8P_2$: C 42.65, H 2.51, N 9.95%; found: C 42.57, H 2.55, N 9.86%. IR (KBr disc, cm^{-1}): 3081 (*w*), 3005 (*w*), 1593 (*s*), 1467 (*m*), 1307 (*m*), 845 (*s*), 657 (*m*).

Crystal data

$[Ag_2(C_{20}H_{14}N_4)_2](PF_6)_2$
M_r = 1126.38
Monoclinic, $C2/c$
a = 20.454 (3) Å
b = 15.749 (3) Å
c = 14.603 (3) Å
β = 120.050 (4)°
V = 4071.9 (12) Å^3
Z = 4

D_x = 1.837 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3734 reflections
θ = 2.3–23.6°
μ = 1.14 mm^{-1}
T = 295 (2) K
Block, colorless
0.25 × 0.20 × 0.15 mm

Data collection

Bruker SMART APEX area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
$T_{\min}$ = 0.709, $T_{\max}$ = 0.848
17 230 measured reflections

4656 independent reflections
3706 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.034
$\theta_{\max}$ = 27.5°
$h = -25 \rightarrow 26$
$k = -20 \rightarrow 20$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.203
S = 1.17
4656 reflections
301 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0875P)^2 + 15.7707P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.68 e Å^{-3}
$\Delta\rho_{\min}$ = −0.62 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ag1—N1$^{\rm i}$	2.112 (5)	Ag1′—N2	2.374 (4)
Ag1—N4	2.351 (5)	Ag1′—N3	2.643 (5)
Ag1—N9′	2.483 (5)	Ag1′—N4$^{\rm i}$	2.220 (4)
Ag1—F1	3.044 (8)	Ag1′—F4	2.829 (4)
Ag1′—N1	2.403 (5)	Ag1′—F5	2.983 (4)
N1$^{\rm i}$—Ag1—N4	149.5 (2)	N2—Ag1′—N3	65.2 (1)
N1$^{\rm i}$—Ag1—N9′	133.8 (2)	N2—Ag1′—N4$^{\rm i}$	140.7 (2)
N1$^{\rm i}$—Ag1—F1	94.6 (2)	N2—Ag1′—F4	76.8 (1)
N4—Ag1—N9′	73.1 (2)	N2—Ag1′—F5	121.6 (1)
N4—Ag1—F1	97.4 (2)	N3—Ag1′—N4$^{\rm i}$	85.3 (2)
N9′—Ag1—F1	94.6 (2)	N3—Ag1′—F4	85.2 (1)
N1—Ag1′—N2	71.4 (2)	N3—Ag1′—F5	112.1 (1)
N1—Ag1′—N3	135.6 (2)	N4$^{\rm i}$—Ag1′—F4	128.3 (2)
N1—Ag1′—N4$^{\rm i}$	137.2 (2)	N4$^{\rm i}$—Ag1′—F5	92.7 (1)
N1—Ag1′—F4	76.4 (2)	F4—Ag1′—F5	46.0 (1)
N1—Ag1′—F5	83.0 (2)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

The Ag atom of the $[(C_{20}H_{14}N_4)_2Ag_2]^{2+}$ dication is disordered over two sites, and the disorder refined to an approximate 2:1 ratio. Arising from the disorder, atom N2, which is coordinated to the Ag1 atom, was refined as a pair of N2 and C2′ atoms sharing the same position.

Similarly, atom C9 was also refined as a pair of C9 and N9′ atoms. The populations of the carbon-bound H atoms were those of the parent atoms. The displacement parameters of the unprimed and primed atoms were made equal to one another. The disorder necessitated all C—C bonds to be restrained to 1.39 (1) Å to prevent a wide range of C—C lengths. H atoms were placed in calculated positions [C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C)] and were included in the refinement in the riding-model approximation.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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