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4,4'-[[[(2,2'-Bipyridine)-5,5'-dicarbonyl]bis(azane-diyl)]bis(1-methylpyridin-1-ium) bis[hexafluorido-phosphate(V)] acetonitrile disolvate

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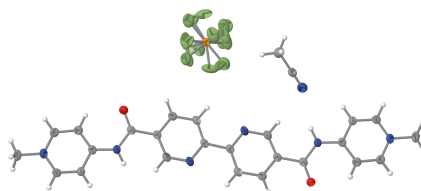
Keywords: crystal structure; redox-active 2,2-bipyridine derivative.

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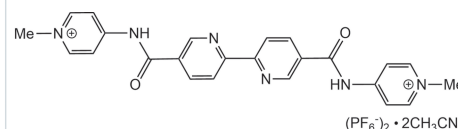
Structural data: full structural data are available from iucrdata.iucr.org

The new redox-active title compound, $C_{24}H_{22}N_6O_2^{2+} \cdot 2PF_6^{-} \cdot 2C_2H_3N$, a 2,2-bipyridine derivative tethered to two *N*-methylpyridinium moieties as electron reservoirs, was synthesized and structurally characterized by 1H NMR spectroscopy and single-crystal X-ray diffractometry. The asymmetric unit comprises one half of the divalent bpy cation together with a $[PF_6]^{-}$ anion and a CH_3CN molecule. The cation is completed by inversion symmetry. The crystal structure features hydrogen-bonding and π - π interactions.

3D view



Chemical scheme



Structure description

2,2'-Bipyridine (bpy) or 1,10-phenanthroline (phen) derivatives have been widely adopted to study various bpy- or phen-ligated transition-metal complexes for a variety of purposes. One of their most remarkable properties lies in the suitably energy-leveled $\pi^*(bpy \text{ or phen})$ -based LUMO, resulting in attractive photochemical and electrochemical properties derived from the redox-active bpy or phen moieties. The $[Ru(bpy \text{ or phen})_3]^{2+}$ family is an important example allowing researchers to advance the knowledge of photochemical and photophysical properties of the 3MLCT (triplet metal-to-ligand charge transfer) excited states and their applications to photo-induced electron transfer reactions, especially artificial photosynthetic reactions driven by such photosensitizers.

For example, our previous studies on hybrid molecular systems consisting of an $[Ru(bpy)_2(phen)]^{2+}$ chromophore and an H_2 -evolving $Pt(bpy)$ catalyst demonstrated a rational strategy to finely tune intramolecular electron-transfer efficiency together with the associated photocatalytic H_2 evolution performance (Ozawa *et al.*, 2006; Masaoka *et al.*, 2010; Suneesh *et al.*, 2014). Our studies on the homogeneous water or CO_2 reduction catalysis have highlighted the importance of raising the electron density at the metal *d* orbitals based on such ligand-based reduction. For example, the $Ni(bpy)(dithiolene)$ H_2 evolution catalyst was shown to significantly accelerate its proton abstraction rate upon



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bpy-based reduction (Koshiba *et al.*, 2019). In general, the performance of cobalt porphyrin CO₂ reduction catalysts was found to largely rely on the porphyrin-based reductions in order to trigger the CO₂-binding step, which requires a formal two-electron reduction of CO₂ to afford a CO₂²⁻-ligated intermediate (Call *et al.*, 2019; Zhang *et al.*, 2019, 2021). A more recent study on Rh(Cp*)(bpy) CO₂ reduction catalysts further evidenced the inevitable role of an Rh(H)(Cp*)(bpy⁻) intermediate in order to gain a great enhancement in its hydricity to transfer a hydride to CO₂ to yield a formate anion (Lee *et al.*, 2024).

In addition to the role of ligand-based reductions, we have also investigated the rate enhancement factors by tethering multiple electron reservoir sites to the ligand coordinated to the catalytically active metal. The Pt(bpy)Cl₂ catalysts tethered to multiple methyl viologen (*i.e.*, *N,N'*-dimethyl-4,4'-bipyridinium) pendants were shown to accelerate the overall photocatalytic H₂ evolution performance (Kitamoto *et al.*, 2014, 2016). The cobalt tetrakis(*N*-methylpyridinium-*n*-yl) porphyrin (*n* = 2,4) CO₂ reduction catalysts were also found to exhibit high catalytic efficiencies by accumulation of multiple electrons (Zhang *et al.*, 2019, 2021).

With the above issues in mind, a new bpy ligand was designed and synthesized to further explore the role of tethered electron reservoir sites. The two methylpyridinium moieties covalently bonded at the 5,5'-positions of the 2,2'-bipyridine unit in the title solvated salt, **I**, are expected to serve as additional redox-active sites upon coordinating a catalytically active metal, such as platinum, rhodium, *etc.* As previously described for the cobalt tetrakis(*N*-methylpyridinium-4-yl)porphyrin catalyst, the two pyridinium moieties linked at both ends of **I** are expected to cooperatively accept electrons using the π -conjugated system. Methylpyridinium pendants as cationic moieties will also facilitate water solubility of catalysts fabricated from **I**. Indeed, a preliminary study on the single-molecular photocatalytic H₂ evolution activity of Pt(**I**)Cl₂ revealed that it exhibits a higher catalytic rate compared to a control having no methylpyridinium pendants (*i.e.*, Pt(5,5'-dicarboxy-2,2'-bipyridine), the details of which will be separately reported elsewhere.

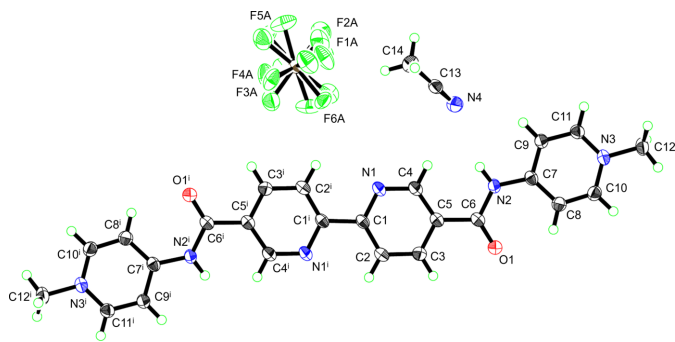


Figure 1
ORTEP diagram of **I** with the atom-labeling scheme, where atoms are drawn using the 50% probability displacement ellipsoids for the non-hydrogen atoms. Labels for the minor component of the disordered atoms were omitted for clarity. Symmetry code: (i) $-x + 1, -y + 1, -z$.

Table 1
Selected bond lengths (Å).

O1—C6	1.215 (2)	C1—C1 ⁱ	1.491 (4)
N1—C4	1.335 (3)	C2—C3	1.386 (3)
N1—C1	1.342 (3)	C3—C5	1.391 (3)
N2—C6	1.373 (2)	C4—C5	1.388 (3)
N2—C7	1.387 (2)	C5—C6	1.500 (3)
N3—C11	1.339 (2)	C7—C8	1.392 (3)
N3—C10	1.352 (3)	C7—C9	1.400 (3)
N3—C12	1.477 (3)	C8—C10	1.362 (3)
N4—C13	1.133 (3)	C9—C11	1.366 (3)
C1—C2	1.390 (3)	C13—C14	1.461 (3)

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

One half of the divalent bpy cation together with a [PF₆]⁻ anion and a CH₃CN molecule is found in the asymmetric unit of **I**. The half cationic fragment is bonded to the neighboring fragment through a crystallographic inversion center to give the whole cationic part of the ligand (Fig. 1), resulting in an almost planar geometry of the central bipyridyl moiety. The central bond distance is expressed by C1—C1ⁱ = 1.491 (4) Å [symmetry code: (i) $-x + 1, -y + 1, -z$] (Table 1). The two independent pyridyl planes possess a planar geometry with an r.m.s. deviation of 0.011 Å for the N1/C1—C5 plane and 0.006 Å for the N3/C7—C11 plane. Although the dihedral angle between these two pyridyl planes is relatively small [*i.e.*, 1.1 (1)°], they do not form a coplanar geometry because of the twists given by the $-C(=O)N-$ plane connecting the two planes. The dihedral angles of the $-C(=O)N-$ plane with regard to the N1/C1—C5 and N3/C7—C11 planes are 11.2 (2) and -12.3 (2)°, respectively. In other words, the six atoms in one pyridyl plane (*e.g.*, N1/C1—C5) are on average shifted out from the other pyridyl plane (*e.g.*, N3/C7—C11) by 0.33 (2) Å.

On the other hand, the crystal packing mode is somewhat unique in that the cationic and anionic components respectively form two-dimensional slabs growing parallel to the *ab* plane, electrostatically consolidating the crystal based on the alternate stacks of oppositely charged two-dimensional slabs (Fig. 2). The acetonitrile molecules are involved in the anionic slabs comprised of the [PF₆]⁻ anions (Fig. 3). The cationic slabs are consolidated by one-dimensional π - π stacking of the

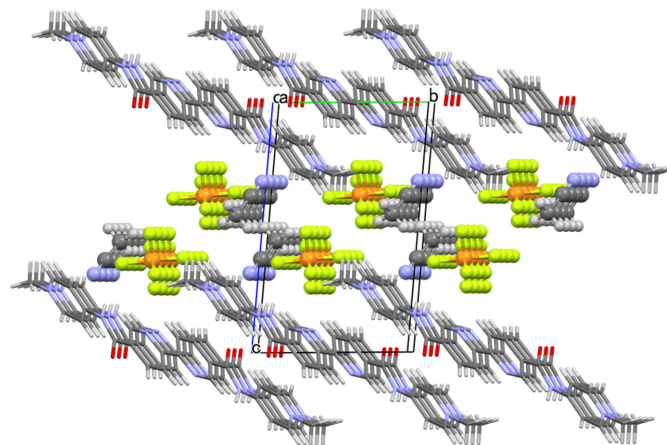


Figure 2
Crystal packing of **I**, viewed along the *a* axis in the range $-1 < a < 2$. Minor disordered PF₆ moieties are omitted for clarity.

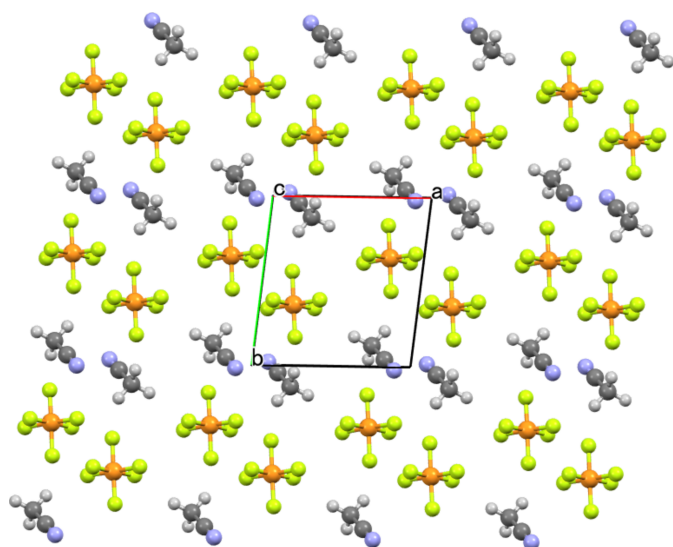


Figure 3
The anionic slab including the acetonitrile molecules, viewed along the c axis, where the a and b axes are given in the vertical and horizontal directions. Minor disordered PF_6 moieties are omitted for clarity.

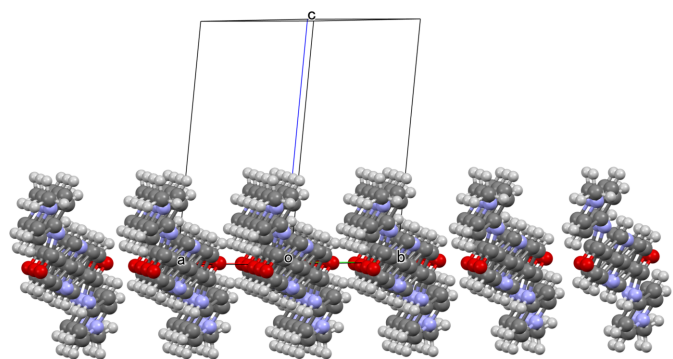


Figure 4
The cationic slab viewed along $[110]$, showing that the 1-D chains are grown by the π - π stacking along this vector with the inter-chain interactions formed along $[1\bar{1}0]$.

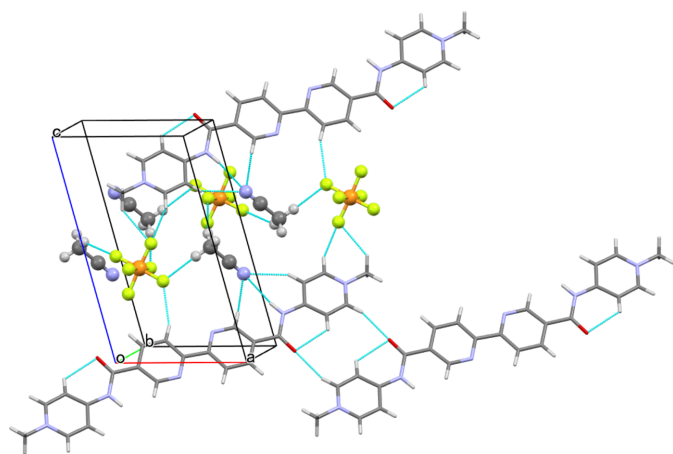


Figure 5
Partial crystal packing of **I**, viewed along the b axis, showing hydrogen-bonding interactions as dotted lines. Minor disordered PF_6 moieties are omitted for clarity.

Table 2
Hydrogen-bond geometry ($\text{\AA}$, $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N2}-\text{H2N}\cdots\text{F3C}^{\text{ii}}$	0.89 (3)	2.11 (3)	2.70 (2)	123 (3)
$\text{N2}-\text{H2N}\cdots\text{N4}$	0.89 (3)	2.47 (3)	3.309 (2)	157 (3)
$\text{C2}-\text{H2}\cdots\text{F6B}^{\text{i}}$	0.95	2.25	3.037 (7)	139
$\text{C4}-\text{H4}\cdots\text{N4}$	0.95	2.45	3.389 (3)	172
$\text{C8}-\text{H8}\cdots\text{O1}$	0.95	2.26	2.838 (3)	118
$\text{C9}-\text{H9}\cdots\text{N4}$	0.95	2.59	3.440 (3)	150
$\text{C10}-\text{H10}\cdots\text{O1}^{\text{iii}}$	0.95	2.26	3.176 (2)	162
$\text{C11}-\text{H11}\cdots\text{F1A}^{\text{iv}}$	0.95	2.29	2.981 (4)	129
$\text{C11}-\text{H11}\cdots\text{F4A}^{\text{v}}$	0.95	2.48	3.020 (6)	116
$\text{C11}-\text{H11}\cdots\text{F6A}^{\text{v}}$	0.95	2.48	2.957 (4)	111
$\text{C11}-\text{H11}\cdots\text{F1B}^{\text{iv}}$	0.95	2.46	3.268 (8)	143
$\text{C11}-\text{H11}\cdots\text{F1C}^{\text{v}}$	0.95	2.36	3.21 (2)	150
$\text{C12}-\text{H12A}\cdots\text{F4C}^{\text{vi}}$	0.98	2.46	3.19 (2)	131
$\text{C12}-\text{H12B}\cdots\text{F1A}^{\text{iv}}$	0.98	2.54	3.348 (4)	139
$\text{C12}-\text{H12B}\cdots\text{F5B}^{\text{iv}}$	0.98	2.33	3.272 (7)	160
$\text{C14}-\text{H14A}\cdots\text{F6A}$	0.98	2.53	3.465 (4)	161
$\text{C14}-\text{H14A}\cdots\text{F1B}$	0.98	2.50	3.264 (10)	134
$\text{C14}-\text{H14A}\cdots\text{F6C}$	0.98	2.27	3.24 (2)	172
$\text{C14}-\text{H14B}\cdots\text{F2A}^{\text{vii}}$	0.98	2.43	3.397 (5)	171
$\text{C14}-\text{H14B}\cdots\text{F2B}^{\text{vii}}$	0.98	2.36	3.334 (13)	176
$\text{C14}-\text{H14B}\cdots\text{F2C}^{\text{vii}}$	0.98	2.05	2.941 (14)	151
$\text{C14}-\text{H14C}\cdots\text{F5A}^{\text{ii}}$	0.98	2.47	3.176 (4)	129

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x+1, y, z$; (iii) $-x+3, -y+2, -z$; (iv) $-x+2, -y+2, -z+1$; (v) $x+1, y+1, z$; (vi) $x+2, y+1, z$; (vii) $-x+1, -y+2, -z+1$.

divalent cations together with the hydrophobic interactions formed among the 1-D chains (Fig. 4). The 1-D chains grow along the $[110]$ direction, while the inter-chain associations perpendicularly grow along the $[1\bar{1}0]$ direction. The separation between π -stacked planes between the one-dimensionally aligned cations is estimated as $3.45(2) \text{ \AA}$ by the results of mean-plane calculations.

The O atom of the amide is involved in two hydrogen bonds with $\text{C8}-\text{H8}$ and $\text{C10}^{\text{iii}}-\text{H10}^{\text{iii}}$ [symmetry code: (iii) $-x+3, -y+2, z$], exhibiting $\text{C}\cdots\text{O}$ distances of $2.838(3)$ and $3.176(2) \text{ \AA}$, respectively (Table 2, Fig. 5). The N atom of the acetonitrile is involved in three hydrogen bonds with $\text{N2}-\text{H2N}$, $\text{C4}-\text{H4}$, and $\text{C9}-\text{H9}$ with $\text{N}\cdots\text{N}$ and $\text{C}\cdots\text{N}$ distances of $3.309(2)$, $3.389(3)$ and $3.440(3) \text{ \AA}$, respectively (Table 2, Fig. 5).

Synthesis and crystallization

Synthesis of I: $N^5, N^{5'}$ -Di(pyridin-4-yl)-2,2'-bipyridine-5,5'-dicarboxamide was prepared by following a literature procedure (Jacobs & Hardie, 2012). A solution of $N^5, N^{5'}$ -di(pyridin-4-yl)-2,2'-bipyridine-5,5'-dicarboxamide (0.16 g, 0.39 mmol) and iodomethane (0.19 ml, 3.0 mmol) in acetonitrile (70 ml) was refluxed for 24 h. The resulting pale-brown precipitate was collected by filtration, washed with acetonitrile ($3 \times 6 \text{ ml}$), and dried *in vacuo*. The iodide salt of the product was then dissolved in water (*ca* 50 ml) followed by addition of an excess of $(\text{NH}_4)[\text{PF}_6]$ (0.68 g, 4.2 mmol) to give the final product in the form of its hemihydrate as a pale-brown solid, which was collected by filtration, washed with water ($3 \times 17 \text{ ml}$), and dried *in vacuo* (yield: 0.20 g, 70%). ^1H NMR (400 MHz, CD_3CN): $\delta/\text{p.p.m.} = 4.18$ (s, 6H), 8.28 (d, 4H, $J = 7.0 \text{ Hz}$), 8.45 (d, 4H, $J = 7.4 \text{ Hz}$), 8.48 (dd, 2H, $J = 8.3, 2.4 \text{ Hz}$), 8.70 (d, 2H, J

= 8.3 Hz), 9.27 (*d*, 2H, *J* = 2.4 Hz), 10.01 (*s*, 2H). Analysis calculated for C₂₄H₂₂N₆O₂F₁₂P₂·0.5H₂O (725.42): C 39.74, H 3.20, N 11.59; found: C 39.63, H 3.01, N 11.51 (%).

Single crystals suitable for the single-crystal X-ray diffraction were grown by vapor diffusion. The above hemihydrate form of the [PF₆][−] salt dissolved in a minimum amount of acetonitrile was sealed within a screw vial under the vapor of diisopropylether. Upon standing overnight at room temperature, dark-brown plates gradually formed and were collected by filtration. The crystals filtered were relatively stable under ambient conditions and did not lose luster for at least several days.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The [PF₆][−] ion was found to be disordered over three sites with site occupation factors of 0.654 (3), 0.291 (3) and 0.0546 (18). Since there was no disorder problem at the central P atom, only the six F atoms were located over three sites (F1A–F6A, F1B–F6B, and F1C–F6C) and refined anisotropically. The refinement of these 18 disordered F atoms were carried out using SADI and SIMU commands of *SHELXL*. The adjacent F–F distances within the individual site were restrained to be equal using SADI, and the P–F distances were restrained to be common. Moreover, the anisotropic displacement parameters of the disordered atoms were restrained to be similar using SIMU.

Acknowledgements

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Table 3

Experimental details.

Crystal data	
Chemical formula	C ₂₄ H ₂₂ N ₆ O ₂ ²⁺ ·2PF ₆ [−] ·2C ₂ H ₃ N
<i>M_r</i>	798.52
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.7661 (2), 8.1535 (3), 13.3262 (5)
α , β , γ (°)	93.392 (3), 102.488 (3), 95.435 (3)
<i>V</i> (Å ³)	817.40 (5)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ^{−1})	0.25
Crystal size (mm)	0.41 × 0.38 × 0.14
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2024)
<i>T_{min}</i> , <i>T_{max}</i>	0.471, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	10914, 3677, 2834
<i>R_{int}</i>	0.044
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.048, 0.123, 1.09
No. of reflections	3677
No. of parameters	351
No. of restraints	1144
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ^{−3})	0.37, −0.35

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXT2018/2* (Sheldrick, 2015a), *KENX* (Sakai, 2025), *SHELXL2019/2* (Sheldrick, 2015b), *KENX* (Sakai, 2025), *ORTEP II* (Johnson, 1976), *TEXSAN* (Molecular Structure Corporation, 2001) and *Mercury* (Macrae et al., 2020).

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full crystallographic data

IUCrData (2025). **10**, x250517 [<https://doi.org/10.1107/S2414314625005176>]

4,4'-{[(2,2'-Bipyridine)-5,5'-dicarbonyl]bis(azanediyl)}bis(1-methylpyridin-1-ium) bis[hexafluoridophosphate(V)] acetonitrile disolvate

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4,4'-{[(2,2'-Bipyridine)-5,5'-dicarbonyl]bis(azanediyl)}bis(1-methylpyridin-1-ium) bis[hexafluoridophosphate(V)] acetonitrile disolvate

Crystal data

$C_{24}H_{22}N_6O_2^{2+} \cdot 2PF_6^- \cdot 2C_2H_3N$

$M_r = 798.52$

Triclinic, $P\bar{1}$

$a = 7.7661$ (2) Å

$b = 8.1535$ (3) Å

$c = 13.3262$ (5) Å

$\alpha = 93.392$ (3)°

$\beta = 102.488$ (3)°

$\gamma = 95.435$ (3)°

$V = 817.40$ (5) Å³

$Z = 1$

$F(000) = 406$

$D_x = 1.622$ Mg m⁻³

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

Cell parameters from 4689 reflections

$\theta = 2.7$ – 28.3°

$\mu = 0.25$ mm⁻¹

$T = 100$ K

Prism, brown

$0.41 \times 0.38 \times 0.14$ mm

Data collection

XtaLAB Synergy, Dualflex, HyPix
diffractometer

Radiation source: micro-focus sealed X-ray tube

Mirror monochromator

Detector resolution: 10.0000 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2024)

$T_{\min} = 0.471$, $T_{\max} = 1.000$

10914 measured reflections

3677 independent reflections

2834 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.044$

$\theta_{\max} = 29.6^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -9 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -14 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.048$

$wR(F^2) = 0.123$

$S = 1.09$

3677 reflections

351 parameters

1144 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0695P)^2 + 0.5331P]$

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

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

$\Delta\rho_{\max} = 0.37$ e Å⁻³

$\Delta\rho_{\min} = -0.35$ e Å⁻³

Special details

Refinement. All H atoms, except for H2N, were placed in idealized positions (methyl C—H = 0.98 Å and aromatic C—H = 0.95 Å) and included in the refinement in a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{methyl C})$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$. Only nitrogen-bound H atom (H2N) was refined isotropically with a fixed isotropic displacement parameter ($U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$).

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
P1	0.21563 (6)	0.64060 (6)	0.37256 (4)	0.02504 (17)	
F1A	0.3516 (5)	0.6623 (6)	0.4791 (3)	0.0672 (13)	0.654 (3)
F2A	0.2511 (8)	0.8319 (5)	0.3589 (4)	0.0421 (11)	0.654 (3)
F3A	0.0840 (4)	0.6143 (4)	0.2600 (2)	0.0609 (9)	0.654 (3)
F4A	0.1824 (8)	0.4450 (5)	0.3815 (5)	0.0482 (12)	0.654 (3)
F5A	0.0563 (4)	0.6665 (4)	0.4234 (3)	0.0514 (8)	0.654 (3)
F6A	0.3769 (4)	0.6091 (4)	0.3167 (3)	0.0464 (8)	0.654 (3)
F1B	0.3948 (10)	0.6197 (12)	0.4536 (6)	0.057 (2)	0.291 (3)
F2B	0.2841 (17)	0.8322 (11)	0.3722 (11)	0.055 (3)	0.291 (3)
F3B	0.0365 (7)	0.6698 (8)	0.2980 (5)	0.0461 (15)	0.291 (3)
F4B	0.1475 (16)	0.4554 (11)	0.3801 (10)	0.054 (3)	0.291 (3)
F5B	0.1342 (11)	0.6971 (10)	0.4707 (5)	0.0646 (19)	0.291 (3)
F6B	0.3012 (11)	0.5969 (12)	0.2820 (5)	0.065 (2)	0.291 (3)
F1C	0.342 (3)	0.539 (3)	0.4504 (15)	0.063 (5)	0.0546 (18)
F2C	0.285 (3)	0.802 (2)	0.4481 (15)	0.060 (4)	0.0546 (18)
F3C	0.088 (3)	0.741 (3)	0.2974 (15)	0.065 (5)	0.0546 (18)
F4C	0.152 (3)	0.479 (2)	0.2969 (15)	0.055 (4)	0.0546 (18)
F5C	0.064 (2)	0.596 (3)	0.4324 (17)	0.057 (5)	0.0546 (18)
F6C	0.370 (2)	0.684 (3)	0.3140 (17)	0.061 (5)	0.0546 (18)
O1	1.16857 (18)	0.84347 (18)	−0.01190 (11)	0.0331 (4)	
N1	0.6300 (2)	0.6666 (2)	0.08593 (13)	0.0313 (4)	
N2	1.1375 (2)	0.9356 (2)	0.14668 (13)	0.0283 (4)	
N3	1.5859 (2)	1.2694 (2)	0.25358 (13)	0.0276 (4)	
N4	0.8997 (2)	1.0188 (3)	0.31784 (15)	0.0381 (5)	
C1	0.5868 (2)	0.5513 (2)	0.00584 (14)	0.0245 (4)	
C2	0.6944 (3)	0.5290 (2)	−0.06365 (15)	0.0267 (4)	
H2	0.657801	0.448885	−0.120957	0.032*	
C3	0.8559 (3)	0.6259 (2)	−0.04778 (15)	0.0259 (4)	
H3	0.931993	0.613397	−0.094126	0.031*	
C4	0.7863 (3)	0.7586 (3)	0.10044 (16)	0.0311 (5)	
H4	0.817968	0.840171	0.157134	0.037*	
C5	0.9049 (3)	0.7416 (2)	0.03710 (14)	0.0247 (4)	
C6	1.0819 (3)	0.8428 (2)	0.05392 (14)	0.0250 (4)	
C7	1.2920 (3)	1.0428 (2)	0.17970 (15)	0.0258 (4)	
C8	1.4345 (3)	1.0520 (3)	0.13156 (16)	0.0292 (4)	
H8	1.431905	0.979342	0.072716	0.035*	
C9	1.3044 (3)	1.1501 (3)	0.26752 (15)	0.0292 (5)	
H9	1.210315	1.146108	0.302866	0.035*	
C10	1.5775 (3)	1.1657 (3)	0.16923 (16)	0.0305 (5)	

H10	1.673548	1.172358	0.135459	0.037*
C11	1.4520 (3)	1.2606 (3)	0.30231 (15)	0.0292 (4)
H11	1.459698	1.332626	0.362209	0.035*
C12	1.7409 (3)	1.3945 (3)	0.29059 (18)	0.0357 (5)
H12A	1.838140	1.366523	0.258886	0.054*
H12B	1.779023	1.396335	0.365756	0.054*
H12C	1.708218	1.503564	0.271681	0.054*
C13	0.8309 (3)	0.9568 (3)	0.37464 (17)	0.0325 (5)
C14	0.7408 (3)	0.8760 (3)	0.44701 (19)	0.0457 (6)
H14A	0.622944	0.825099	0.410193	0.069*
H14B	0.728513	0.958103	0.501048	0.069*
H14C	0.810483	0.790600	0.478350	0.069*
H2N	1.068 (4)	0.925 (4)	0.192 (2)	0.069*

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

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
P1	0.0254 (3)	0.0250 (3)	0.0236 (3)	0.0021 (2)	0.0033 (2)	0.0018 (2)
F1A	0.059 (2)	0.094 (4)	0.0334 (16)	−0.018 (2)	−0.0151 (14)	0.0217 (18)
F2A	0.052 (2)	0.0252 (18)	0.053 (2)	0.0034 (13)	0.0191 (19)	0.0070 (14)
F3A	0.0591 (19)	0.071 (2)	0.0362 (15)	−0.0266 (16)	−0.0125 (12)	0.0090 (13)
F4A	0.045 (2)	0.0259 (16)	0.085 (3)	0.0057 (13)	0.036 (2)	0.0163 (16)
F5A	0.0469 (16)	0.0370 (15)	0.080 (2)	0.0065 (13)	0.0356 (15)	0.0024 (15)
F6A	0.0506 (16)	0.0312 (13)	0.066 (2)	−0.0042 (13)	0.0376 (15)	−0.0025 (15)
F1B	0.052 (4)	0.040 (4)	0.062 (5)	0.005 (3)	−0.023 (3)	0.001 (3)
F2B	0.045 (4)	0.037 (5)	0.075 (6)	0.002 (3)	−0.001 (4)	−0.004 (4)
F3B	0.035 (3)	0.033 (3)	0.058 (4)	−0.007 (2)	−0.015 (3)	0.010 (3)
F4B	0.036 (4)	0.043 (5)	0.075 (5)	0.003 (3)	−0.007 (4)	0.013 (4)
F5B	0.088 (5)	0.067 (4)	0.056 (4)	0.028 (4)	0.045 (4)	0.011 (3)
F6B	0.102 (6)	0.064 (4)	0.036 (4)	0.018 (5)	0.030 (4)	−0.002 (3)
F1C	0.062 (8)	0.052 (8)	0.065 (8)	0.007 (8)	−0.005 (8)	0.000 (8)
F2C	0.066 (7)	0.054 (7)	0.059 (7)	−0.001 (7)	0.011 (7)	0.012 (7)
F3C	0.064 (8)	0.055 (8)	0.068 (8)	−0.003 (8)	0.002 (8)	0.003 (8)
F4C	0.054 (7)	0.055 (7)	0.051 (7)	−0.009 (7)	0.008 (7)	0.003 (7)
F5C	0.057 (8)	0.043 (8)	0.069 (8)	−0.002 (8)	0.012 (8)	0.000 (8)
F6C	0.065 (8)	0.054 (8)	0.063 (8)	−0.002 (8)	0.015 (8)	−0.006 (8)
O1	0.0314 (8)	0.0376 (9)	0.0294 (8)	−0.0029 (6)	0.0096 (6)	−0.0037 (6)
N1	0.0289 (9)	0.0338 (10)	0.0265 (9)	−0.0054 (7)	0.0015 (7)	−0.0051 (7)
N2	0.0252 (8)	0.0331 (10)	0.0242 (9)	−0.0057 (7)	0.0047 (7)	−0.0002 (7)
N3	0.0249 (8)	0.0269 (9)	0.0283 (9)	−0.0017 (7)	0.0017 (7)	0.0031 (7)
N4	0.0350 (10)	0.0433 (11)	0.0353 (10)	0.0047 (8)	0.0073 (8)	−0.0016 (9)
C1	0.0269 (10)	0.0223 (10)	0.0207 (9)	0.0016 (8)	−0.0018 (7)	0.0022 (7)
C2	0.0309 (10)	0.0232 (10)	0.0231 (10)	0.0024 (8)	0.0008 (8)	−0.0003 (8)
C3	0.0271 (10)	0.0264 (10)	0.0240 (10)	0.0050 (8)	0.0039 (8)	0.0030 (8)
C4	0.0315 (11)	0.0313 (11)	0.0268 (11)	−0.0031 (9)	0.0031 (8)	−0.0042 (8)
C5	0.0278 (10)	0.0219 (10)	0.0224 (10)	0.0019 (8)	0.0009 (8)	0.0039 (7)
C6	0.0283 (10)	0.0218 (10)	0.0229 (10)	0.0034 (8)	0.0011 (8)	0.0027 (7)
C7	0.0270 (10)	0.0249 (10)	0.0232 (10)	0.0004 (8)	0.0009 (8)	0.0037 (8)

C8	0.0277 (10)	0.0307 (11)	0.0289 (11)	0.0045 (8)	0.0053 (8)	0.0011 (8)
C9	0.0275 (10)	0.0324 (11)	0.0261 (10)	−0.0024 (8)	0.0056 (8)	0.0007 (8)
C10	0.0263 (10)	0.0346 (12)	0.0310 (11)	0.0034 (9)	0.0071 (8)	0.0028 (9)
C11	0.0310 (10)	0.0317 (11)	0.0237 (10)	−0.0005 (9)	0.0051 (8)	0.0017 (8)
C12	0.0295 (11)	0.0345 (12)	0.0395 (12)	−0.0075 (9)	0.0049 (9)	0.0024 (9)
C13	0.0258 (10)	0.0359 (12)	0.0327 (11)	0.0039 (9)	0.0024 (9)	−0.0076 (9)
C14	0.0398 (13)	0.0549 (16)	0.0428 (14)	−0.0025 (11)	0.0144 (11)	−0.0008 (11)

Geometric parameters (Å, °)

O1—C6	1.215 (2)	C7—C9	1.400 (3)
N1—C4	1.335 (3)	C8—C10	1.362 (3)
N1—C1	1.342 (3)	C9—C11	1.366 (3)
N2—C6	1.373 (2)	C13—C14	1.461 (3)
N2—C7	1.387 (2)	P1—F6B	1.538 (7)
N2—H2N	0.89 (3)	P1—F5A	1.559 (3)
N3—C11	1.339 (2)	P1—F1A	1.565 (3)
N3—C10	1.352 (3)	P1—F4B	1.568 (8)
N3—C12	1.477 (3)	P1—F3B	1.573 (5)
N4—C13	1.133 (3)	P1—F3C	1.574 (11)
C1—C2	1.390 (3)	P1—F4C	1.580 (11)
C1—C1 ⁱ	1.491 (4)	P1—F5C	1.585 (11)
C2—C3	1.386 (3)	P1—F2A	1.586 (4)
C3—C5	1.391 (3)	P1—F2C	1.587 (11)
C4—C5	1.388 (3)	P1—F6C	1.590 (11)
C5—C6	1.500 (3)	P1—F1B	1.596 (7)
C7—C8	1.392 (3)		
C4—N1—C1	117.76 (17)	C11—C9—C7	119.88 (18)
C6—N2—C7	127.37 (16)	N3—C10—C8	121.53 (18)
C6—N2—H2N	117 (2)	N3—C11—C9	121.25 (18)
C7—N2—H2N	115.5 (19)	N4—C13—C14	179.4 (2)
C11—N3—C10	119.84 (17)	F5A—P1—F1A	92.52 (19)
C11—N3—C12	120.07 (17)	F6B—P1—F4B	92.8 (5)
C10—N3—C12	120.08 (17)	F6B—P1—F3B	92.3 (4)
N1—C1—C2	122.80 (17)	F4B—P1—F3B	91.9 (5)
N1—C1—C1 ⁱ	115.9 (2)	F3C—P1—F4C	90.4 (7)
C2—C1—C1 ⁱ	121.3 (2)	F3C—P1—F5C	90.3 (7)
C3—C2—C1	118.74 (18)	F4C—P1—F5C	91.0 (7)
C2—C3—C5	118.93 (18)	F5A—P1—F2A	92.5 (2)
N1—C4—C5	123.50 (19)	F1A—P1—F2A	90.6 (2)
C4—C5—C3	118.20 (18)	F3C—P1—F2C	90.4 (7)
C4—C5—C6	123.78 (17)	F4C—P1—F2C	178.4 (8)
C3—C5—C6	118.01 (17)	F5C—P1—F2C	90.3 (7)
O1—C6—N2	122.54 (17)	F3C—P1—F6C	90.6 (8)
O1—C6—C5	121.43 (17)	F4C—P1—F6C	89.2 (7)
N2—C6—C5	116.03 (16)	F5C—P1—F6C	179.1 (9)
N2—C7—C8	124.85 (18)	F2C—P1—F6C	89.4 (7)

N2—C7—C9	117.34 (17)	F6B—P1—F1B	90.9 (4)
C8—C7—C9	117.81 (18)	F4B—P1—F1B	89.8 (5)
C10—C8—C7	119.68 (19)	F3B—P1—F1B	176.3 (4)
C4—N1—C1—C2	−2.5 (3)	C4—C5—C6—N2	11.2 (3)
C4—N1—C1—C1 ⁱ	178.6 (2)	C3—C5—C6—N2	−169.84 (17)
N1—C1—C2—C3	2.3 (3)	C6—N2—C7—C8	−12.5 (3)
C1 ⁱ —C1—C2—C3	−178.8 (2)	C6—N2—C7—C9	166.98 (19)
C1—C2—C3—C5	0.1 (3)	N2—C7—C8—C10	178.0 (2)
C1—N1—C4—C5	0.3 (3)	C9—C7—C8—C10	−1.5 (3)
N1—C4—C5—C3	2.0 (3)	N2—C7—C9—C11	−178.67 (19)
N1—C4—C5—C6	−179.0 (2)	C8—C7—C9—C11	0.9 (3)
C2—C3—C5—C4	−2.1 (3)	C11—N3—C10—C8	0.4 (3)
C2—C3—C5—C6	178.83 (17)	C12—N3—C10—C8	−178.3 (2)
C7—N2—C6—O1	1.0 (3)	C7—C8—C10—N3	0.8 (3)
C7—N2—C6—C5	−177.87 (18)	C10—N3—C11—C9	−1.1 (3)
C4—C5—C6—O1	−167.70 (19)	C12—N3—C11—C9	177.6 (2)
C3—C5—C6—O1	11.3 (3)	C7—C9—C11—N3	0.4 (3)

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

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

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N2—H2N $\cdots$ F3C ⁱⁱ	0.89 (3)	2.11 (3)	2.70 (2)	123 (3)
N2—H2N $\cdots$ N4	0.89 (3)	2.47 (3)	3.309 (2)	157 (3)
C2—H2 $\cdots$ F6B ⁱ	0.95	2.25	3.037 (7)	139
C4—H4 $\cdots$ N4	0.95	2.45	3.389 (3)	172
C8—H8 $\cdots$ O1	0.95	2.26	2.838 (3)	118
C9—H9 $\cdots$ N4	0.95	2.59	3.440 (3)	150
C10—H10 $\cdots$ O1 ⁱⁱⁱ	0.95	2.26	3.176 (2)	162
C11—H11 $\cdots$ F1A ^{iv}	0.95	2.29	2.981 (4)	129
C11—H11 $\cdots$ F4A ^v	0.95	2.48	3.020 (6)	116
C11—H11 $\cdots$ F6A ^v	0.95	2.48	2.957 (4)	111
C11—H11 $\cdots$ F1B ^{iv}	0.95	2.46	3.268 (8)	143
C11—H11 $\cdots$ F1C ^v	0.95	2.36	3.21 (2)	150
C12—H12A $\cdots$ F4C ^{vi}	0.98	2.46	3.19 (2)	131
C12—H12B $\cdots$ F1A ^{iv}	0.98	2.54	3.348 (4)	139
C12—H12B $\cdots$ F5B ^{iv}	0.98	2.33	3.272 (7)	160
C14—H14A $\cdots$ F6A	0.98	2.53	3.465 (4)	161
C14—H14A $\cdots$ F1B	0.98	2.50	3.264 (10)	134
C14—H14A $\cdots$ F6C	0.98	2.27	3.24 (2)	172
C14—H14B $\cdots$ F2A ^{vii}	0.98	2.43	3.397 (5)	171
C14—H14B $\cdots$ F2B ^{vii}	0.98	2.36	3.334 (13)	176
C14—H14B $\cdots$ F2C ^{vii}	0.98	2.05	2.941 (14)	151
C14—H14C $\cdots$ F5A ⁱⁱ	0.98	2.47	3.176 (4)	129

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $x+1, y, z$; (iii) $-x+3, -y+2, -z$; (iv) $-x+2, -y+2, -z+1$; (v) $x+1, y+1, z$; (vi) $x+2, y+1, z$; (vii) $-x+1, -y+2, -z+1$.