

Crystal and Molecular Structure of Tris(2,2'-bipyridyl)osmium(II) Bis(hexafluorophosphate)

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Abstract. $[\text{Os}(\text{C}_{10}\text{H}_8\text{N}_2)_3](\text{PF}_6)_2$, $M_r = 948.70$, trigonal, $P\bar{3}c1$, $a = 10.790$ (3), $c = 16.365$ (4) Å, $V = 1650$ (1) Å³, $T = 295$ K, $D_x = 1.91$ Mg m⁻³, $Z = 2$, $\mu = 40.6$ cm⁻¹, $F(000) = 920$, Mo $K\alpha$ ($\lambda = 0.71069$ Å), $R = 0.0326$ for 935 unique observed $[|F| \geq 3\sigma(F)]$ reflections and 78 parameters. $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$ has approximately octahedral coordination, the Os sits on a site of $\bar{3}$ (D_3) symmetry with Os—N distances of 2.062 (4) Å, N—Os—N *trans* angles of 172.4 (2)°, N—Os—N bite angles of 77.9 (2)°, and the remainder of N—Os—N angles ranging from 89.3 (2) to 96.6 (2)°. The ordered PF_6 anions sit on sites of threefold (C_3) symmetry with average bond distances of 1.566 (8) Å. The title compound is isostructural with $[\text{Ru}(\text{bpy})_3](\text{PF}_6)_2$.

Experimental. $[\text{Os}(\text{bpy})_3](\text{PF}_6)_2$ (bpy = 2,2'-bipyridine) was prepared by a modification of the procedure of Burstall, Dwyer & Gyarfus (1950), and its properties have been reported elsewhere (Richter & Brewer, 1991). Recrystallization was accomplished using the technique of vapor diffusion (Stout & Jensen, 1968), with the compound dissolved in acetonitrile and using ether as the precipitating solvent. The crystals were large, thick, purple hexagons and had to be cut for the X-ray experiment.

An irregularly shaped crystal with dimensions of $0.41 \times 0.25 \times 0.17$ mm was selected for data collection on a Syntex P2, diffractometer, with graphite monochromator, upgraded to Nicolet R3 specifications (Campana, Shepard & Litchman, 1981). Lattice constants from 25 reflections in the range $26 < 2\theta < 36^\circ$. Data were collected with ω scans (1°); two check reflections monitored every 96 reflections (034 and $3\bar{3}4$) show no systematic excursions; 1523 total reflections to $2\theta = 55^\circ$, 935 unique with $R_{\text{merge}} = 0.044$; hkl ranges, $0 \leq h \leq 15$, $0 \leq k \leq 15$, $-22 \leq l \leq 22$. Empirical ψ scan absorption corrections (program XEMP in SHELXTL) applied assuming an ellipsoidally shaped crystal (transmission range: 0.702–0.971).

The structure solution was obtained *via* the direct methods routine SOLV in the SHELXTL crystallo-

graphic program package and refinement also used that set of programs (Sheldrick, 1985). The c -axis axial photograph showed no symmetry and thus a trigonal crystal class was assumed. The systematic absences of hhl for l odd correspond to the space groups $P\bar{3}c1$ or $P3c1$. The choice of the centrosymmetric group, $P\bar{3}c1$, was indicated by intensity statistics and confirmed by successful solution and refinement. A difference synthesis based on the Os position, obtained by placing the Os on a site of $\bar{3}$ symmetry, yielded the C, N, P and F positions. The final refinement included positional parameters on all non-H atoms. All non-H atoms were refined using anisotropic thermal parameters, H atoms were constrained to ideal locations (C—H and N—H = 0.96 Å) and assigned isotropic thermal parameters of 1.2 times the associated atoms. The large F thermal parameters indicate a large amount of librational disorder in the PF_6 anions.

The final refinement resulted in $R = 0.0326$ [$|F| > 3\sigma(F)$ data] and 0.0465 (all data), and $wR = 0.0318$ (3σ data set) where $w = 1/[\sigma^2(F) + g(F)^2]$, with $g = 0.00013$. The goodness of fit as 1.545, with parameter changes in the final cycle of least squares of $|\Delta/\sigma|(\text{mean}) = 0.001$ and $|\Delta/\sigma|(\text{max}) = 0.003$. The largest peak on the final difference map was 0.75 e Å^{-3} near P(1), while the most negative excursion was -0.75 e Å^{-3} . Atomic coordinates are listed in Table 1 and bond distances and angles are given in Table 2. A view of the structure is shown in Fig. 1.†

Related literature. Os^{II} polypyridine compounds have been shown to undergo facile photoinitiated electron transfer (Creutz, Chou, Netzel, Okumura & Sutin, 1980), oxidative and reductive quenching (Kober, Marshall, Dressick, Sullivan, Caspar & Meyer, 1985) and are capable of functioning as electron-transfer

† Tables of data collection parameters, anisotropic thermal parameters, H-atom positions and isotropic thermal parameters, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54267 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for [Os(bpy)₃](PF₆)₂

	x	y	z	U*
Os	0	0	2500	41 (1)
N	822 (4)	1897 (5)	3138 (3)	48 (2)
C(1)	433 (5)	2848 (5)	2874 (3)	50 (2)
C(2)	834 (6)	4101 (6)	3304 (3)	63 (3)
C(3)	1650 (8)	4398 (7)	3993 (4)	71 (3)
C(4)	2067 (7)	3444 (7)	4246 (4)	66 (3)
C(5)	1655 (7)	2229 (6)	3809 (3)	59 (3)
P(1)	6667	3333	3698 (2)	76 (1)
F(1)	5414 (7)	3195 (9)	3157 (4)	139 (4)
F(2)	7929 (8)	3512 (9)	4258 (4)	163 (5)

* The equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

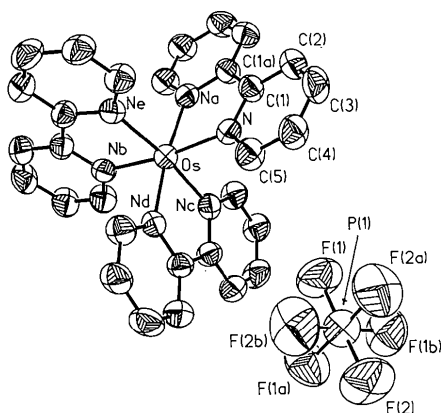


Fig. 1. A view of the title compound showing thermal ellipsoids.

photocatalysts (Lumpkin, Kober, Worl, Murtaza & Meyer, 1990), features which make them desirable for incorporation into solar-energy conversion schemes. The title compound is isostructural with [Ru(bpy)₃](PF₆)₂, the structure of which has been reported previously (Rillema & Jones, 1979).

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Structure of a Ferrocenylalkyl–Aminomalonamide Derivative

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Abstract. *N*-Benzoyl-*N*-(1-ferrocenyl-2,2-dimethyl-1-propyl)amino-*N*',*N*'-di(1,1,3,3-tetramethyl-1-butyl)-malonamide, C₄₁H₆₁FeN₃O₃, $M_r = 699.81$, triclinic,

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Table 2. Bond distances (\AA) and angles ($^\circ$) for [Os(bpy)₃](PF₆)₂

Atom labels are defined in the figure.			
Os—N	2.062 (4)	C(2)—C(3)	1.367 (9)
N—C(1)	1.359 (9)	C(3)—C(4)	1.377 (13)
N—C(5)	1.349 (7)	C(4)—C(5)	1.359 (9)
C(1)—C(2)	1.387 (8)	P(1)—F(1)	1.560 (8)
C(1)—C(1a)	1.470 (9)	P(1)—F(2)	1.572 (9)
N—Os—N(a)	96.6 (1)	C(2)—C(3)—C(4)	119.1 (6)
N—Os—N(c)	89.3 (2)	C(3)—C(4)—C(5)	119.4 (6)
N(b)—Os—N(c)	77.9 (2)	N—C(5)—C(4)	122.6 (7)
N—Os—N(d)	172.4 (2)	F(1)—P(1)—F(2)	178.2 (5)
Os—N—C(1)	116.6 (3)	F(1)—P(1)—F(1a)	91.0 (3)
Os—N—C(5)	125.1 (5)	F(2)—P(1)—F(1a)	90.9 (5)
C(1)—N—C(5)	118.3 (5)	F(2)—P(1)—F(1b)	88.3 (3)
N—C(1)—C(2)	120.8 (5)	F(1)—P(1)—F(2a)	88.8 (5)
N—C(1)—C(1a)	114.3 (4)	F(2)—P(1)—F(2a)	89.4 (4)
C(2)—C(1)—C(1a)	124.9 (5)	F(1)—P(1)—F(2b)	90.8 (3)
C(1)—C(2)—C(3)	119.8 (7)		

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$P\bar{1}$, $a = 8.564$ (1), $b = 12.000$ (2), $c = 20.111$ (2) \AA , $\alpha = 79.35$ (1), $\beta = 78.93$ (1), $\gamma = 77.64$ (1) $^\circ$, $V = 1958.9$ \AA^3 , $Z = 2$, $D_x = 1.186$ g cm⁻³, $\lambda(\text{Mo } K\alpha) =$