

Table 1. Atomic coordinates and equivalent isotropic thermal parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
Ir	0.258880 (20)	-0.08396 (4)	0.192210 (20)	0.03610 (23)
P(2)	0.16359 (18)	0.0920 (3)	0.24370 (18)	0.0438 (15)
Cl(1)	0.35738 (18)	-0.0608 (3)	0.33320 (18)	0.0515 (16)
Cl(2)	0.34329 (21)	0.0982 (4)	0.13402 (21)	0.0648 (19)
P(1)	0.36319 (19)	-0.2549 (4)	0.14951 (21)	0.0545 (18)
S	0.17658 (22)	-0.0676 (4)	0.05226 (19)	0.0592 (18)
Cl(3)	0.04967 (23)	-0.1759 (5)	0.06788 (25)	0.085 (3)
O(1)	0.2188 (7)	-0.1410 (11)	-0.0163 (5)	0.078 (6)
C(2)	0.1859 (7)	-0.2261 (13)	0.2331 (7)	0.046 (6)
O(2)	0.1477 (6)	-0.3067 (9)	0.2589 (6)	0.063 (6)
C(111)	0.3076 (9)	-0.4027 (12)	0.0913 (8)	0.059 (7)
C(112)	0.3641 (9)	-0.5219 (12)	0.0760 (8)	0.062 (8)
C(121)	0.4326 (11)	-0.3339 (22)	0.2425 (13)	0.135 (16)
C(122)	0.3755 (16)	-0.4124 (21)	0.3022 (11)	0.126 (16)
C(131)	0.4327 (14)	-0.1731 (21)	0.0628 (15)	0.065 (14)
C(132)	0.5196 (16)	-0.251 (3)	0.0512 (17)	0.089 (17)
C(133)	0.4801 (20)	-0.220 (4)	0.1215 (22)	0.051 (11)
C(134)	0.476 (3)	-0.191 (5)	0.028 (3)	0.061 (12)
C(211)	0.2302 (8)	0.2228 (13)	0.3102 (8)	0.061 (8)
C(212)	0.1753 (10)	0.3368 (14)	0.3458 (9)	0.075 (9)
C(221)	0.0853 (8)	0.1828 (12)	0.1596 (8)	0.056 (7)
C(222)	0.1335 (9)	0.2889 (13)	0.1054 (9)	0.071 (9)
C(231)	0.0826 (8)	0.0238 (14)	0.3152 (8)	0.058 (7)
C(232)	0.1250 (9)	-0.0363 (15)	0.4011 (8)	0.068 (8)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Ir—P(1)	2.399 (3)	P(2)—C(231)	1.829 (12)
Ir—P(2)	2.398 (3)	S—Cl(3)	2.168 (5)
Ir—Cl(1)	2.426 (3)	S—O(1)	1.462 (10)
Ir—Cl(2)	2.391 (3)	C(2)—O(2)	1.065 (14)
Ir—S	2.304 (3)	C(111)—C(112)	1.458 (18)
Ir—C(2)	1.898 (11)	C(121)—C(122)	1.51 (3)
P(1)—C(111)	1.822 (13)	C(131)—C(132)	1.50 (3)
P(1)—C(121)	1.798 (19)	C(133)—C(134)	1.45 (6)
P(1)—C(131)	1.932 (22)	C(211)—C(212)	1.507 (19)
P(1)—C(133)	1.84 (3)	C(221)—C(222)	1.544 (18)
P(2)—C(211)	1.823 (12)	C(231)—C(232)	1.486 (18)
P(2)—C(221)	1.825 (12)		
P(2)—Ir—P(1)	175.67 (10)	Ir—P(2)—C(221)	117.0 (4)
Cl(1)—Ir—P(1)	88.78 (10)	Ir—P(2)—C(231)	112.3 (4)
Cl(2)—Ir—P(1)	92.30 (11)	C(111)—P(1)—C(121)	102.2 (7)
P(1)—Ir—S	94.12 (11)	C(111)—P(1)—C(131)	103.6 (8)
P(1)—Ir—C(2)	89.1 (3)	C(111)—P(1)—C(133)	113.7 (11)
P(2)—Ir—Cl(1)	87.05 (10)	C(121)—P(1)—C(131)	114.7 (9)
P(2)—Ir—Cl(2)	86.46 (10)	C(211)—P(2)—C(221)	106.7 (6)
P(2)—Ir—S	89.79 (11)	C(211)—P(2)—C(231)	105.3 (6)
P(2)—Ir—C(2)	92.3 (3)	C(221)—P(2)—C(231)	101.4 (6)
Cl(1)—Ir—Cl(2)	88.99 (10)	Ir—S—Cl(3)	102.44 (17)
Cl(1)—Ir—S	169.49 (11)	Ir—S—O(1)	113.9 (4)
Cl(1)—Ir—C(2)	94.1 (3)	Cl(3)—S—O(1)	106.5 (4)
Cl(2)—Ir—S	80.81 (11)	Ir—C(2)—O(2)	177.0 (10)
Cl(2)—Ir—C(2)	176.6 (3)	P(1)—C(111)—C(112)	118.7 (9)
S—Ir—C(2)	96.0 (3)	P(1)—C(121)—C(122)	112.8 (14)
Ir—P(1)—C(111)	114.9 (4)	P(1)—C(131)—C(132)	113.4 (16)
Ir—P(1)—C(121)	113.4 (6)	P(1)—C(133)—C(134)	110.2 (26)
Ir—P(1)—C(131)	107.7 (7)	P(2)—C(211)—C(212)	116.3 (9)
Ir—P(1)—C(133)	124.8 (10)	P(2)—C(221)—C(222)	114.1 (8)
Ir—P(2)—C(211)	112.9 (4)	P(2)—C(231)—C(232)	115.8 (9)

Experimental. The title compound was prepared by oxidative addition of SOCl_2 to $[\text{IrCl}(\text{CO})(\text{PEt}_3)_2]$; crystals were obtained from $\text{CH}_2\text{Cl}_2/\text{hexane}$. A colourless irregular column-shaped crystal, $0.25 \times 0.30 \times 0.75$ mm, was mounted on a CAD-4 diffractometer (graphite-monochromated $\text{Mo K}\alpha$ X-radiation). Cell parameters were refined against the positions of 25 centred reflections with $28 < 2\theta < 30^\circ$. For data collection $T = 183$ K, ω - 2θ -scan mode, $2\theta_{\text{max}} = 50^\circ$, h - $17 \rightarrow 17$, k $0 \rightarrow 11$, l $0 \rightarrow 18$. Two standard reflections varied randomly by $\pm 7\%$

but did not indicate significant crystal movement or decay. Of the 4130 reflections collected, 3739 were unique ($R_{\text{int}} 0.043$) and 2803 with $F > 6\sigma(F)$ were used for structure solution (from a Patterson synthesis followed by iterative cycles of least-squares refinement and difference Fourier synthesis) and refinement [using full-matrix least squares on F (*SHELX76*; Sheldrick, 1976)]. At isotropic convergence, corrections (maximum 1.448, minimum 0.771) for absorption were applied empirically using *DIFABS* (Walker & Stuart, 1983). One of the ethyl groups on P(1) was disordered: a model involving two partly occupied orientations [C(131) and C(132) 0.53, C(133) and C(134) 0.47] was applied. Anisotropic thermal parameters were refined for all non-H atoms except C atoms in the minor component of the disorder; H atoms were included in fixed calculated positions; no secondary-extinction parameter. At final convergence, $R = 0.0448$, $wR = 0.0504$, $S = 1.11$ for 208 parameters, $(\Delta/\sigma)_{\text{max}} = 0.03$ in final cycle, maximum and minimum residues in the final ΔF synthesis were 1.98 and -2.35 e \AA^{-3} , respectively. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000137F^2$ gave satisfactory agreement analyses. Scattering factors were inlaid (Sheldrick, 1976) except for Ir (Cromer & Mann, 1968). Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, while selected bond lengths and angles appear in Table 2.* The atom-numbering scheme for the molecule is shown in Fig. 1, which was generated using the version of *ORTEP* included in the *GX* crystallographic program system (Mallinson & Muir,

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55093 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA0103]

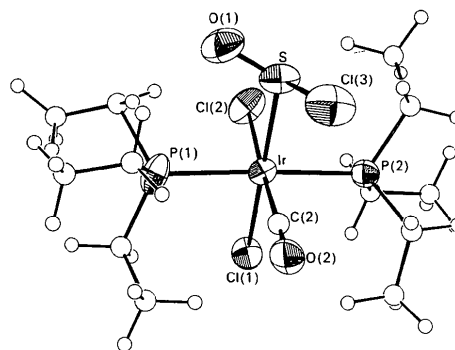


Fig. 1. A general view of the molecule showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level, except those of C and H which have artificial radii of 0.15 and 0.10 \AA , respectively, for clarity. Only the major component of the disordered ethyl group is shown.

1985). Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

Related literature. Other small molecules such as PF₄Cl, CF₃Br and CF₃I undergo oxidative addition at Ir^I and Rh^I centres and we have determined the structures of some of the resulting Ir^{III} and Rh^{III} products (Blake, Cockman, Ebsworth, Henderson, Holloway, Pilkington & Rankin, 1987; Blake, Ebsworth, Holloway & Rieland, 1992).

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Structure of Pentakis(*N,N*-dimethylformamide)dioxouranium(VI) Tetrafluoroborate

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Abstract. [UO₂(C₃H₇NO)₅](BF₄)₂, $M_r = 809.11$, monoclinic, *C2/c*, $a = 21.077$ (5), $b = 13.296$ (3), $c = 11.525$ (2) Å, $\beta = 112.24$ (2)°, $V = 2989$ (1) Å³, $Z = 4$, $D_x = 1.798$ g cm⁻³, $\lambda(\text{Mo } K\alpha_1) = 0.71073$ Å, $\mu = 52.34$ cm⁻¹, $F(000) = 1560$, $T = 295$ K, $R = 0.029$ for 1935 independent observed reflections with $I > 3\sigma(I)$. The structure consists of packed UO₂(dmf)₅ cations [dmf = (CH₃)₂NCHO] and BF₄ anions. The linear UO₂ group is equatorially surrounded by five O atoms belonging to dmf molecules. The uranyl distance of 1.762 (3) Å is typical for the UO₂ group and the equatorial U—O distances fall in the range 2.334 (5)–2.383 (3) Å.

Experimental. A yellow single crystal of dimensions 0.35 × 0.35 × 0.30 mm, grown during the reaction between tetrafluoroboric acid and UO₃ in aqueous dmf solution, was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite monochromator. Lattice parameters were determined by least-squares procedure from the setting angles of 25 reflections with $\theta = 8$ –12°. Data were collected up to $2\theta = 50^\circ$ and measured for $0 \leq h \leq 25$, $0 \leq k \leq 15$, $-13 \leq l \leq 13$, with ω - 2θ scans, ω -scan width $(0.80 + 0.35 \tan \theta)^\circ$ at 1.54–10° min⁻¹. Three standard reflections measured every hour (151, 731, 423) showed a loss of intensity of 4.7% in 36 h; a linear correction was applied. Lorentz–polarization correction and an empirical absorption correction using the program *DIFABS* (Walker & Stuart, 1983), maximum and minimum transmission 0.801 and

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1.298, were applied. 2832 reflections were measured, 2626 unique ($R_{\text{int}} = 0.024$), of which 1935 with $I > 3\sigma(I)$ were used in structure solution and refinement. The structure was solved by the heavy-atom method and refined by full-matrix least-squares procedures based on F , with anisotropic thermal parameters. 178 parameters were refined; H atoms not introduced. All calculations were performed on a MicroVAX II computer with the *Enraf–Nonius Structure Determination Package* (Frenz, 1985). The U atom lies on the diad axis, as do the O and N atoms of a dmf molecule [O(2) and N(2) introduced in refinements with an occupation factor of 0.5]. Atomic scattering factors including anomalous-scattering contributions were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Minimized function: $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o/\sigma^2(I)$ with $\sigma^2(I) = [\sigma^2(I_c) + (pF_o)^2]$, $p = 0.04$. Final $R = 0.029$, $wR = 0.034$, $S = 3.60$, $(\Delta/\sigma)_{\text{max}} = 0.01$, highest peak in the final difference Fourier map = $0.499 \text{ e } \text{Å}^{-3}$. The final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.* Bond lengths and angles are listed in Table 2. A perspective view of the molecular structure with the atom-numbering scheme is shown in Fig. 1.

* Lists of structure factors, anisotropic thermal parameters, and bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55132 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: DU0327]