Preparation and Structure of Azidopentafluorotungsten(VI)

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Azidotrimethylsilane reacts with excess of WF_6 to give the title compound. This yellow compound, which decomposes explosively at 63 °C, has a monoclinic unit cell with $a = 5.240(8)$, $b = 9.662(12)$, $c = 10.835(8)$ Å, $\beta = 102.4(1)°$, space group $P2_1/c$, and $Z = 4$. Using 1 122 X-ray data collected on a two-circle diffractometer, refinement converged at R 0.076. The average W–F distance is 1.836 Å; other distances are W–N(1) 1.584(21), N(1)–N(2) 1.254(31), and N(2)–N(3) 1.102(36) Å. The W–N(1)–N(2) angle is 157.4(23)°.

IT was shown several years ago that one or more of the fluorine atoms in tungsten hexafluoride may be replaced by chlorine,[1,2] or by alkoxy-,[3] aroxy-,[3,4] or diethylamino-groups.[5,6] Azido-derivatives of fluorides have not been reported, although corresponding derivatives of tungsten hexachloride and of other metal chlorides [7-9] have been known for some time. In this paper we report the first preparation of an azido-fluoride, $WF_5(N_3)$, and the determination of its crystal structure.

EXPERIMENTAL

Reagents and Apparatus.—Tungsten hexafluoride (Ozark Mahoning Co.) was stored for several days over dried sodium fluoride in a heavy walled Kel-F tube closed by a Kel-F valve before use. Azidotrimethylsilane (P.C.R. Inc.) was vacuum distilled twice, rejecting the first and last fractions. Genetron 113 (1,1,2-trichlorotrifluoroethane, $C_2Cl_3F_3$) (Fluka A.G.) was purified by a trap-to-trap distillation, dried over P_2O_5, and stored over a molecular sieve. The experiments were performed in pre-seasoned Pyrex tubes (capacity 10 cm³) attached through glass–Teflon valves to a conventional metal vacuum line.

Preparation of Azidopentafluorotungsten(VI).—Genetron solvent (1 cm³) was added by vacuum distillation to azidotrimethylsilane (0.1 g) in such a way as to ensure that no undissolved reagent remained on the walls of the reaction vessel. A five-fold excess of tungsten hexafluoride (1.5 g) was transferred to the reaction vessel, held at −180 °C, by vacuum distillation, and the mixture was allowed to warm up slowly to room temperature. Reaction was completed by warming to $\leqslant 45$ °C and allowing the solvent (and excess of WF_6) to reflux to a cooled collar on the Pyrex tube for about 3 h. After cooling to 25 °C the excess of WF_6 and most of the solvent were removed in a static vacuum, care being taken to avoid the solid drying out at this stage. The reaction vessel was transferred to an efficient dry-box, and the moist solid was spread out on a clean watchglass to allow the remaining solvent to evaporate. **CAUTION:** It is particularly important not to attempt to dry the compound under a dynamic vacuum as it is liable to detonate under such conditions. The azidopentafluorotungsten(VI) was characterized by its mass spectrum at 58 °C (Figure 1) and by the ^{19}F n.m.r. spectrum of its solution in Genetron (Table 1).

Other Reactions of $Si(CH_3)_3(N_3)$ *with Fluorides.*—**CAUTION:** Tungsten hexafluoride reacted with excess of $Si(CH_3)_3(N_3)$ in Genetron using a similar procedure to that outlined above to give a yellow-orange solution which detonated at room temperature. The reaction of $Si(CH_3)_3(N_3)$ with an excess of MoF_6 yielded, in Genetron solution, a yellow solid, assumed to be $MoF_5(N_3)$, which decomposed at −10 °C.

Structure Determination.—Yellow crystals were obtained on standing the product of the reaction between an excess of WF_6 and $Si(CH_3)_3(N_3)$ in Genetron for several days. The crystals which formed on the reactor walls just above the solution were found to be suitable. The crystal chosen for data collection had approximate dimensions 0.28 × 0.11 × 0.03 mm and was sealed into a pre-seasoned (ClF_3), evacuated, glass capillary. Approximate cell dimensions were obtained from Weissenberg photographs taken with Cu-K_α radiation and refined from optimized setting angles for zero- and upper-layer reflections on a Weissenberg diffractometer using Mo-K_α radiation.

Crystal data. F_5N_3W, $M = 320.9$, Monoclinic, $a = 5.240(8)$, $b = 9.662(12)$, $c = 10.835(8)$ Å, $\beta = 102.4(1)°$, $U = 535.8$ Å³, $D_c = 3.98$ g cm⁻³ for $Z = 4$, $F(000) = 560$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 207 cm⁻¹, space group $P2_1/c$.

Data were collected from layers $h(0\text{—}10)l$ on a Stoe Stadi-2 Weissenberg diffractometer in the quadrants $\pm h,k,l$ using an ω-scan technique.[10] The intensities of reflections with $0.086 < (\sin\theta)/\lambda < 0.7$ Å⁻¹ were measured and a total of 1 122 reflections with $I \geqslant 3\sigma(I)$ was obtained. Routine monitoring of check reflections revealed some crystal decomposition. Accordingly one reflection from each layer was remeasured at the end of the data collection, and the derived layer scale factors were used as a check against subsequent layer scale factors obtained by structure-factor least-squares refinement.

Structure solution and refinement. Calculations were made using the program system SHELX-76 with scattering factors fully corrected for anomalous dispersion.[11] Conventional heavy-atom methods were used to solve the structure, but least-squares refinement using isotropic thermal parameters converged with $R = 0.25$. An absorption correction reduced R to 0.19. Layer scale factors were introduced to allow for crystal decomposition, whereupon the refined values were found to agree closely with those derived from the remeasured reflections and R was reduced to 0.15. With anisotropic thermal parameters for all atoms, refinement converged at $R = 0.076$. Weights were calculated from the expression $1/[\sigma^2(F) + 0.008F^2]$ which gave a satisfactory analysis over $|F_o|$ and $(\sin\theta)/\lambda$, and gave $R' = 0.080$.

Final atomic positional parameters are given in Table 2, interatomic distances and angles in Table 3. Thermal parameters and structure factors are available as Supplementary Publication No. SUP 22861 (6 pp.).†

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

DISCUSSION

TABLE 1

Fluorine-19 n.m.r. data* for WF_5X compounds

	δ/p.p.m.		J/Hz		
Compound	$F_{eq.}$	$F_{ax.}$	M–F	F–F	Ref.
WF_6			44		2
$WF_5(OMe)$	−46	−75	40	66	3
$WF_5(OPh)$	−39	−53	39	64	3
$WClF_5$	16	39	25	73	2
$WF_5(OC_6F_5)$	−20.56	−24.11		70	4, 6
$WF_5(N_3)$	−18	−26	n.o.	68	This work

* Referred to WF_6, a negative chemical shift being on the high-field side. n.o. = Not observed.

TABLE 2

Fractional atomic co-ordinates

Atom	*x*	*y*	*z*
W	0.1510(2)	0.0359(1)	0.2879(1)
F(1)	−0.054(3)	−0.078(3)	0.163(2)
F(2)	−0.153(3)	0.129(2)	0.294(2)
F(3)	0.424(3)	−0.078(2)	0.277(2)
F(4)	0.081(4)	−0.083(2)	0.408(2)
F(5)	0.207(3)	0.135(2)	0.157(2)
N(1)	0.352(4)	0.151(3)	0.407(3)
N(2)	0.483(4)	0.256(3)	0.449(2)
N(3)	0.605(5)	0.343(4)	0.494(3)

Azidopentafluorotungsten(VI) forms a yellow crystalline solid at 25 °C which will not redissolve in Genetron without partial decomposition. The compound is very much less volatile than $WClF_5$, and does not melt below its (explosive) decomposition point at 63 °C. The i.r. spectrum of the solid shows absorptions attributable to the N_3 group at 2 140 and at *ca.* 640 cm^{-1}, and the Raman spectrum of the solution in Genetron also shows an azido-group absorption at 2 157 cm^{-1}. The ^{19}F n.m.r. spectrum in Genetron shows the expected doublet and a poorly resolved quintet (Table 1). Above 63 °C, or when subjected to shock, $WF_5(N_3)$ decomposes explosively to a black solid which analysis shows to have a composition close to WF_3N, but the mass spectrum of this material indicates that it is more likely to be a mixture than a single phase. It has been shown that $WCl_5(N_3)$ loses chlorine and nitrogen on standing in CCl_4 solution at 25 °C, to form WCl_3N,[8] but it seems unlikely that a similar mechanism could operate for $WF_5(N_3)$.

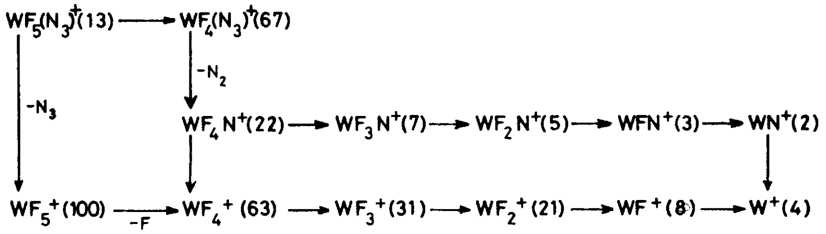

FIGURE 1 Mass spectrum of $WF_5(N_3)$: speculative fragmentation sequence. Intensities based on ^{184}W are given in parentheses

TABLE 3

Bond lengths (Å) and angles (°)

(*a*) Lengths

W–F(1)	1.890(18)	W–F(5)	1.785(16)
W–F(2)	1.843(14)	W–N(1)	1.85(2)
W–F(3)	1.826(17)	N(1)–N(2)	1.25(3)
W–F(4)	1.838(20)	N(2)–N(3)	1.10(4)

(*b*) Angles

F(1)–W–F(2)	87.1(8)	F(3)–W–F(4)	87.1(1.0)
F(1)–W–F(3)	86.2(9)	F(3)–W–F(5)	90.7(9)
F(1)–W–F(4)	88.4(9)	F(3)–W–N(1)	94.1(9)
F(1)–W–F(5)	84.9(9)	F(4)–W–F(5)	173.1(8)
F(1)–W–N(1)	178.6(1.1)	F(4)–W–N(1)	92.9(1.0)
F(2)–W–F(3)	172.1(7)	F(5)–W–N(1)	93.7(1.0)
F(2)–W–F(4)	88.5(8)	W–N(1)–N(2)	157(2)
F(2)–W–F(5)	93.2(8)	N(1)–N(2)–N(3)	175(3)
F(2)–W–N(1)	92.8(9)		

The general shape of the $WF_5(N_3)$ molecule (Figure 2) is as expected. The angle at N(1) is 157° compared with the more usual values of 114° (NH_3)[12] and of 120° (CH_3N_3)[13] found in some covalent azides. It is, however, not necessarily a unique feature, as similar angles are found in certain isothiocyanates [*e.g.* $Si(CH_3)_3(NCS)$, 154°;[14] and CH_3NCS, 142°[15]]. The N(1)–N(2) bond lies in a plane with three fluorine atoms of the same molecule, so that N(2) is oriented towards F(5) rather than between F(5) and either F(3) or F(2). This is presumably the result of packing considerations within the unit cell (Figure 3), since the barrier to rotation about W-N(1) is expected to be low.

The five W–F bond lengths within the molecular unit (Table 3) average 1.836, σ = 0.038 Å, compared with 1.832 in WF_6[16] and 1.836 in $WClF_5$.[17] However, fluorine atom F(5), with the closest intramolecular contact to the azido-group, has the shortest W–F bond length, whilst

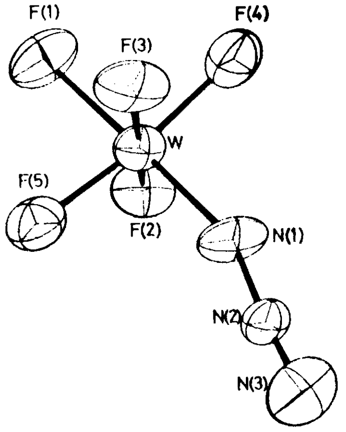

FIGURE 2 Molecular structure showing atomic numbering

F(1), which lies *trans* to the azido-group, has the longest W–F bond length; the remaining W–F bond lengths average 1.836, $\sigma = 0.009$ Å. The N(1)–N(2) and N(2)–N(3) bond lengths are similar to those in other covalent azides. All four equatorial fluorine atoms are bent away from the azido-group; the mean N(1)–W–$F_{eq.}$ angle is 93.4(6)°. Each tungsten atom has six approximately equidistant tungsten neighbours, with W–W distances of 5.10—5.27 Å.

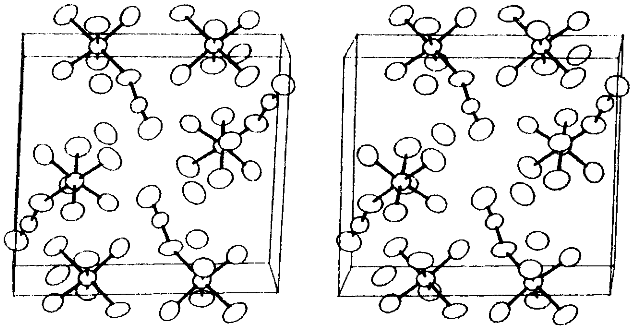

FIGURE 3 Stereoscopic view of the unit-cell contents viewed approximately along *a*

There are no unusually short intramolecular contacts, the shortest being N(2)–F(1) 2.82, N(2)–F(4) 2.98, and F(4)–F(4) 2.82 Å, which approach van der Waals contact. The N(1) atoms lie in an approximate plane of fluorine atoms in the {101} plane.

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