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Photochemical Synthesis of Tungsten Pentafluoride, WF_5

Riane Stene,^[a,b] Benjamin Scheibe,^[a] Sergei I. Ivlev,^[a] Antti J. Karttunen,^[c] Winfried Petry,^[b] and Florian Kraus^{*[a]}

Dedicated to Prof. Dr. Thomas M. Klapötke on the Occasion of his 60th Birthday

Abstract. A new synthetic route for the synthesis of WF_5 utilizing a mercury photosensitized reduction of tungsten hexafluoride with H_2 is described. Crystals of WF_5 were studied using single-crystal X-ray diffraction, resulting in the first-reported crystal structure of WF_5 . Powder X-ray diffraction studied at room-temperature showed the compound was phase-pure. The IR spectrum of WF_5 was re-

investigated and interpreted with the use of solid-state quantum-chemical calculations using the DFT-PBE0 density functional method. The compound synthesized herein was free of HF and moisture but may have contained minute amounts of WOF_4 , that were only observed in the IR spectrum.

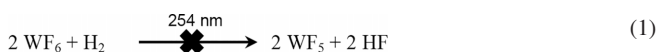
Introduction

Studies describing the synthesis and characterization of tungsten pentafluoride (WF_5) began to appear in the literature in the 1960's and 1970's.^[1–6] However, not much attention has since been given to this pentafluoride. Most likely, the difficulties surrounding the preparation of WF_5 are the reason why comparatively few studies regarding its chemical properties exist. In 1968 and again in 1969, Schröder and Grewe described the first synthesis of WF_5 .^[1,2] To perform this synthesis, a sophisticated and highly specialized apparatus must be used. Briefly, though, tungsten hexafluoride (WF_6) comports with tungsten wire at 500 to 700 °C. This interaction led to the formation of WF_5 , which had to be trapped by cooling specific areas of the apparatus between –50 and –60 °C.

Later, in 1976, O'Donnell and Peel described the preparation of WF_5 through competitive Lewis acid-base reactions.^[5] To perform this synthesis, NaWF_6 was dissolved in anhydrous hydrogen fluoride (aHF) and to this solution a quantity of SbF_5 was given so that NaWF_6 was present in slight excess. A pale-yellow solution was formed at –50 °C, which was decanted

from any precipitate that had formed (NaSbF_6), and the aHF was removed in vacuo at –50 °C. The WF_5 could be further purified by allowing the sample to warm to 0 °C and collecting the sublimed material at –80 °C. Recently, Gerken and co-workers reported on the controlled abstraction of F^- from WF_6 in $\text{C}_5\text{H}_5\text{N}$ using $(\text{CH}_3)_3\text{SiO}_3\text{SCF}_3$, resulting in the $[\text{WF}_5(\text{NC}_5\text{H}_5)_3]^+$ cation, which can be decomposed in $\text{C}_5\text{H}_5\text{N}$ to achieve a controlled reduction to $\text{WF}_5(\text{NC}_5\text{H}_5)_2$.^[7] The synthesis of $\text{WF}_5(\text{NC}_5\text{H}_5)_2$ demonstrates that WF_6 may be reduced under mild conditions.^[7]

Using a wavelength of 254 nm and a fluorine radical scavenger, the synthesis of phase-pure UF_5 and MoF_5 from UF_6 and MoF_6 , respectively, has previously been reported.^[8–10] Curiously, WF_5 has yet to be synthesized by reduction of WF_6 with UV light in the presence of a fluorine radical scavenger. It was the goal of this study to determine if this reaction could be applied for the synthesis of WF_5 . Unfortunately, our initial studies into this reaction were unsuccessful because the reaction described by Equation (1) does not proceed:



This result is not surprising because WF_6 does not absorb UV light above 180 nm.^[11] Our attention then turned to finding a suitable photosensitizer that would allow the reaction described by Equation (1) to proceed.

Mercury photosensitization has played a critical role in the area of photochemistry since the 1970's.^[12] When Hg ($^1\text{S}_0$ ground state) is irradiated with 254 nm light, excited atoms of Hg ($^3\text{P}_1$, Hg^*) are formed having an excitation energy of 112 kcal·mol^{–1}.^[12] When H_2 is present, the Hg^* atoms have enough energy to homolytically break the H–H bond (103 kcal·mol^{–1}).^[12] The H radicals can then further react with other chemical species present in the reaction mixture.

Utilizing the photosensitization of Hg , we have demonstrated that WF_5 may be produced by means of the following reaction, Equation (2):

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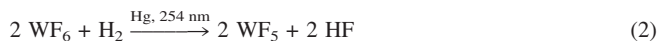
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More details regarding this reaction will be discussed below.

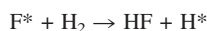
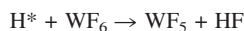
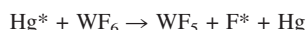
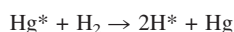
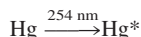
Herein we report upon a new synthetic method for the synthesis of WF_5 using photosensitization. Single-crystal X-ray diffraction leads to the first crystal structure determination of WF_5 . We have also reinvestigated the IR spectrum, the vibrational assignments of which were aided by solid-state quantum-chemical calculations performed on the solid-state structure of WF_5 .

Results and Discussion

Synthesis of WF_5

To synthesize WF_5 , a drop of mercury was added into a perfluoroethylene/perfluoropropylene copolymer (FEP) reaction vessel and WF_6 was condensed into the reaction vessel followed by H_2 addition at liquid nitrogen temperature. The reaction mixture was warmed slowly to room temperature and irradiated with UV light having a wavelength of 254 nm for approximately 15 hours. Afterwards, a brown-yellow sample was obtained that contained yellow single crystals of WF_5 . The volatile species were removed and the WF_5 was collected under an inert atmosphere in a glovebox.

While the exact nature of the reaction mechanism is beyond our current capabilities, it is thought to occur through the formation of hydrogen radicals,^[12] which then react with WF_6 to produce WF_5 . Alternatively, although to a much smaller extent, the Hg^* atoms may react directly with WF_6 to form WF_5 and a fluorine radical, according to Equation (3), Equation (4), Equation (5), Equation (6), Equation (7), and Equation (8). As a side note, the formation of HgF_2 and Hg_2F_2 was not observed, however, the Hg tarnished during reaction but the recovered Hg had a shiny silver luster.



This photosensitization reaction seems dependent on the presence of H_2 , because the reaction does not take place to any appreciable extent under other gaseous atmospheres, such as CO or CO_2 .

Single-Crystal and Powder X-ray Diffraction

As predicted by Edwards,^[3] WF_5 crystallizes in the MoF_5 structure type ($m\bar{3}48$, j^4i^3h), space group $C2/m$ (no. 12) with the lattice parameters of $a = 9.4964(9)$, $b = 14.1820(12)$, $c = 5.0712(5)$ Å, $\beta = 96.778(7)^\circ$, $V = 678.21(11)$ Å³, $Z = 8$, $T = 100$ K. The crystal structure of the compound is characterized by W_4F_{20} molecules formed from tetramerization of WF_5 units (see Figure 1). These molecules may be described by the Niggli formula $\frac{0}{\infty}[\text{WF}_{2/2}\text{F}_{4/1}]$, that is, each tungsten atom has four terminally bound F atoms and two μ_2 -bridging F atoms. Atomic coordinates and equivalent isotropic displacement parameters for WF_5 are reported in Table 1; selected crystallographic data and details of the single-crystal structure determination are given in Table 2.

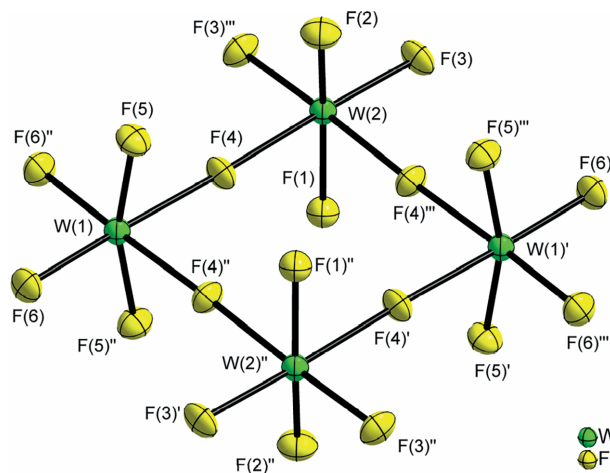


Figure 1. The W_4F_{20} tetramer observed in the solid-state structure of WF_5 . Displacement ellipsoids are shown at a 70 % probability level at 100 K [symmetry transformations for the generation of equivalent atoms: (') $1 -x, 1 -y, 1 -z$; (') $1 -x, y, 1 -z$; (') $x, 1 -y, z$].

Additionally, a powder X-ray diffraction pattern of WF_5 was obtained at room temperature and lattice parameters were determined through Rietveld refinement (Figure 2) to be $a = 9.64431(7)$, $b = 14.32135(10)$, $c = 5.24942(4)$ Å, $\beta = 94.5598(4)^\circ$, $V = 722.753(9)$ Å³. Selected crystallographic data and details of the Rietveld refinement are given in

Table 1. Atomic coordinates and equivalent isotropic displacement parameters U_{iso} at 100 K for WF_5 obtained from single-crystal X-ray diffraction.

Atom	Position	x	y	z	$U_{\text{iso}} / \text{\AA}^2$
W(1)	4h	½	0.70421(2)	½	0.01165(12)
W(2)	4i	0.24126(3)	½	0.75206(5)	0.01162(12)
F(1)	4i	0.3673(6)	½	1.0523(11)	0.0169(11)
F(2)	4i	0.1629(6)	½	0.4062(11)	0.0192(12)
F(3)	8j	0.1276(4)	0.4059(3)	0.8605(8)	0.0185(9)
F(4)	8j	0.3737(4)	0.6009(3)	0.6284(7)	0.0171(8)
F(5)	8j	0.3935(4)	0.6862(3)	0.1804(7)	0.0171(8)
F(6)	8j	0.6182(5)	0.7937(3)	0.3793(9)	0.0177(9)

Table 2. Selected crystallographic data and details of the single-crystal structure determination and Rietveld refinement of WF₅.

	WF ₅ (SCXRD) at 100 K	F ₅ W	WF ₅ (PXRD) at 298 K
Empirical formula		F ₅ W	
Color and appearance	yellow block		yellow-brown powder
Molar mass /g·mol ⁻¹		278.85	
Crystal system		monoclinic	
Space group (no.)		C2/m (12)	
Pearson symbol		mS48	
<i>a</i> /Å	9.4964(9)		9.64431(7)
<i>b</i> /Å	14.1820(12)		14.32135(10)
<i>c</i> /Å	5.0712(5)		5.24942(4)
β /°	96.778(7)		94.5598(4)
<i>V</i> /Å ³	678.21(11)		722.753(9)
<i>Z</i>		8	
$\rho_{\text{calcd.}}$ /g·cm ⁻³	5.462		5.125
λ /Å	0.71073 (Mo- <i>K</i> _α)		1.5406 (Cu- <i>K</i> _{α1})
<i>T</i> /K	100		293
μ /mm ⁻¹	34.040		59.478
θ_{min} /°	2.873		—
θ_{max} /°	31.497		—
2θ range measured /°	—		10.00–94.96
2θ range refined /°	—		10.00–94.96
<i>hkl</i> range	−13 ≤ <i>h</i> ≤ 12; −20 ≤ <i>k</i> ≤ 20; −7 ≤ <i>l</i> ≤ 7		—
<i>R</i> _{int} , <i>R</i> _σ	0.075, 0.039		—
<i>R</i> (<i>F</i>) [<i>I</i> ≥ 2σ(<i>I</i>), all data]	0.028, 0.033		—
<i>wR</i> (<i>F</i> ²) [<i>I</i> ≥ 2σ(<i>I</i>), all data]	0.067, 0.070		—
<i>R</i> _p , <i>wR</i> _p	—		0.027, 0.038
<i>cR</i> _p , <i>cwR</i> _p ^{a)}	—		0.141, 0.121
<i>R</i> _{Bragg} (<i>I</i>)	—		0.021
<i>S</i> (all data)	1.05		2.62
Data, parameter, restraints	1171, 61, 0		5665, 96, 5 ^{b)}
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ /e·Å ⁻³	2.31, −2.07		—

a) Background-corrected R-factors. b) *U*_{iso} of fluorine atoms were constrained to be equal.

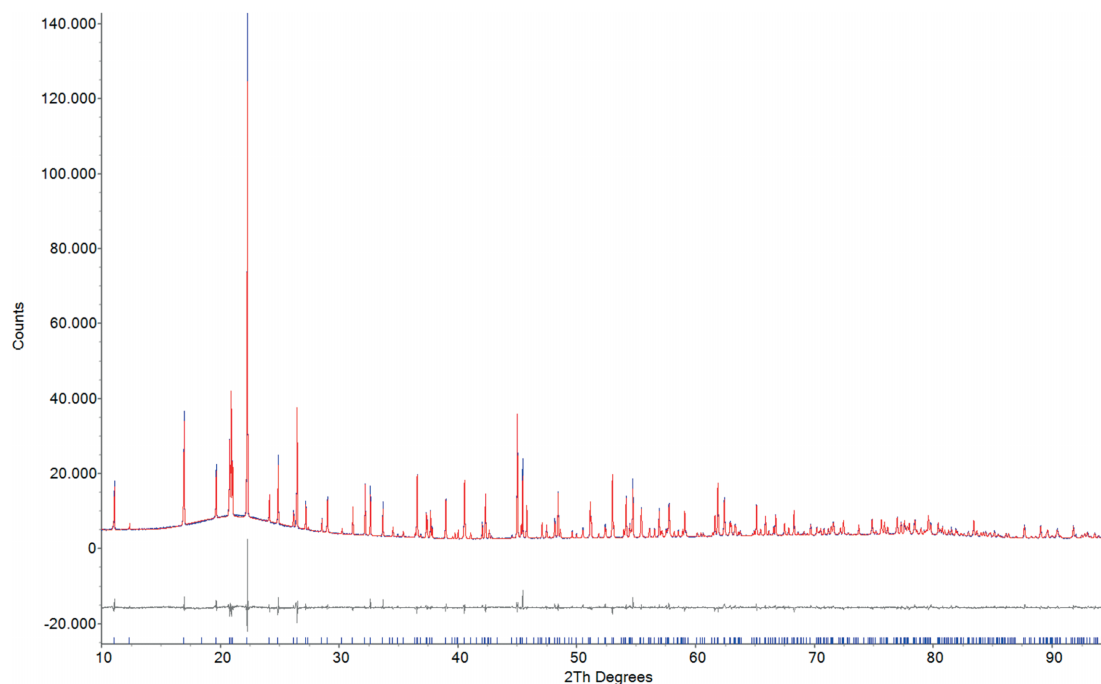


Figure 2. The powder X-ray diffraction pattern of WF₅ measured at 293 K, processed using the TOPAS-Academic program using a Rietveld refinement.^[14] The observed powder diffraction pattern is shown in blue, while the calculated powder diffraction pattern is shown in red. The difference between the observed and calculated patterns is shown by the gray difference curve at the bottom of the schematic.

Table 2. Based on powder X-ray diffraction data, Edwards previously reported the lattice parameters of WF₅ to be $a = 9.61$, $b = 14.26$, $c = 5.23$ Å, $\beta = 94.6^\circ$.^[3] These lattice parameters compare reasonably well and are also nicely repro-

Table 3. Comparison of selected atomic distances observed in the crystal structure of WF_5 with the previously reported atomic distances observed in the isotopic pentafluorides, MoF_5 , NbF_5 , and TaF_5 .

Atom1	Atom2	$d/\text{\AA}$ (WF_5)	$d/\text{\AA}$ (MoF_5) ^[21]	$d/\text{\AA}$ (MoF_5) ^[13]	$d/\text{\AA}$ (NbF_5) ^[15]	$d/\text{\AA}$ (TaF_5) ^[22]
$M(1)$	$M(1)'$	5.7922(6)	5.7776(5)	5.800(6)	5.800(6)	—
$M(2)$	$M(2)'$	5.8009(7)	5.7853(5)	5.860(6)	5.900(6)	—
$M(1)$	$M(2)$	4.0988(4)	4.0881(3)	—	—	—
$M(1)$	$F_t(5)$	1.824(4)	1.8012(13)	1.82(9)	1.78(5)	1.858(10)
$M(1)$	$F_t(6)$	1.846(4)	1.8236(14)	1.89(4)	1.75(2)	1.840(11)
$M(1)$	$\mu\text{-F}(4)$	2.048(4)	2.0423(11)	2.04(4)	2.06(2)	2.073(8)
$M(2)$	$\mu\text{-F}(4)$	2.052(4)	2.0463(11)	2.09(4)	2.07(2)	2.058(8)
$M(2)$	$F_t(1)$	1.822(5)	1.8013(18)	1.69(10)	1.75(5)	1.852(15)
$M(2)$	$F_t(2)$	1.822(5)	1.8011(18)	1.66(10)	1.78(5)	1.881(15)
$M(2)$	$F_t(3)$	1.841(4)	1.8183(13)	1.74(4)	1.78(2)	1.797(9)

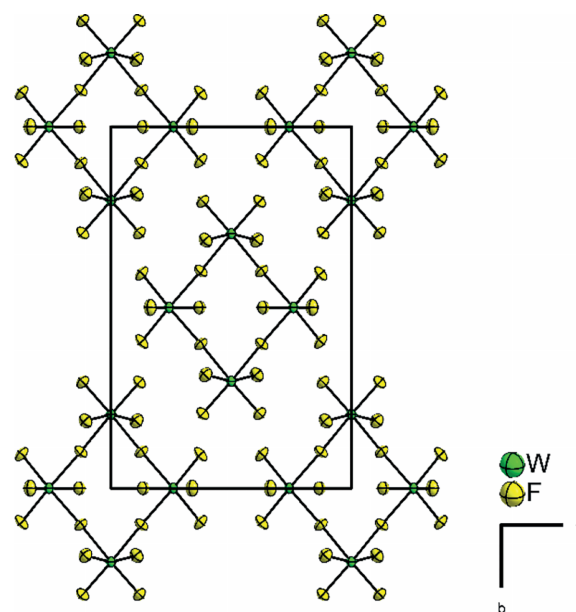
Table 4. Comparison of selected interatomic angles observed in the crystal structure of WF_5 with the previously reported interatomic angles observed in the isotopic pentafluorides, MoF_5 , NbF_5 , and TaF_5 .

	Angle /° (WF_5)	Angle /° (MoF_5) ^[21]	Angle /° (MoF_5) ^[13]	Angle /° (NbF_5) ^[15]	Angle /° (TaF_5) ^[22]
$M(1)-\mu\text{-F}(4)-M(2)$	178.1(2)	178.20(7)	180.0(20)	182.5(20)	172.9(5)
$F_t(5)-M(1)-F_t(5)''$	163.9(3)	162.23(10)	165.8(25)	164.0(25)	164.1(7)
$F_t(6)-M(1)-\mu\text{-F}(4)$	177.76(19)	178.04(6)	—	—	172.7(5)
$F_t(1)-M(2)-\mu\text{-F}(2)$	163.2(3)	161.74(9)	164.7(30)	167.0(25)	161.9(6)
$F_t(3)-M(2)-\mu\text{-F}(4)$	177.75(17)	178.15(6)	—	—	171.5(4)

duced by the solid-state quantum-chemical calculations (see below).

Like the other pentafluorides that crystallize in the MoF_5 structure type (NbF_5 , TaF_5 , MoF_5), the fluorine atoms in WF_5 pack in a distorted cubic close packed array.^[13,15,16] In contrast, the pentafluorides belonging to the RuF_5 structure type (RuF_5 , OsF_5 , RhF_5 , PtF_5), which may be described as corrugated tetramers, have fluorine atoms that pack in a distorted hexagonal close packed array.^[17–20] Additionally, within the MoF_5 structure type, the point symmetry of the M_4F_{20} ($M = \text{Nb}$, Ta , Mo , W) molecule is C_{2h} , with a twofold rotation axis running through both $M(1)$ atoms and the perpendicular mirror plane that bisects the $M(2)$, $F(1)$ and $F(2)$ atoms. In the RuF_5 structure type, the M_4F_{20} ($M = \text{Ru}$, Os , Rh , Pt) molecule has C_i point symmetry.

In WF_5 , there are two crystallographically distinct W atoms – $W(1)$ and $W(2)$ – both of which are coordinated by six fluorine atoms (four terminal fluorine atoms, F_t , and two bridging fluorine atoms, $\mu\text{-F}$) to form octahedron-like coordination polyhedra. The $W-F_t$ distances range between 1.822(5) and 1.846(4) Å, and the $W-\mu\text{-F}$ distances range between 2.048(4) and 2.052(4) Å. The distances to the bridging F atoms are therefore longer, as is expected due to their higher coordination number. The $W(1)-W(2)$ distance is 4.0988(4) Å, the $W(1)-W(1)'$ distance is 5.7921(8) Å, and the $W(2)-W(2)''$ distance is 5.8009(8) Å. Compared to MoF_5 , these distances are slightly longer, as expected due to the slightly larger ionic radius of tungsten. A comparison of selected atomic distances observed in these pentafluorides is reported in Table 3. Another characteristic of the MoF_5 structure type is a nearly linear $M-\mu\text{-F}-M$ angle ($M = \text{Nb}$, Ta , Mo , W). This angle has a value of 178.1(2)° in WF_5 and a reported angle of 178.20(7) for MoF_5 .^[21] In NbF_5 and TaF_5 , this angle is reported to be 182.5(2)° and 172.9(5)°, respectively.^[15,16] A comparison of select interatomic angles observed in WF_5 and in the remain-

**Figure 3.** The crystal structure of WF_5 . Displacement ellipsoids are shown at the 70 % probability level at 100 K.

ing pentafluorides belonging to this structure type is given in Table 4 and the crystal structure of WF_5 is shown in Figure 3.

IR Spectroscopy

An IR spectrum of polycrystalline WF_5 was measured at room temperature in the region of 4000 to 400 cm^{-1} . The IR spectrum shows six bands at approximately 510, 664, 706, 727, 751, and 1048 cm^{-1} . No bands were observed beyond 1100 cm^{-1} indicating that the compound is essentially free of HF and moisture. The band arising at 1048 cm^{-1} is due to the presence of very small amounts of WOF_4 , which was unde-

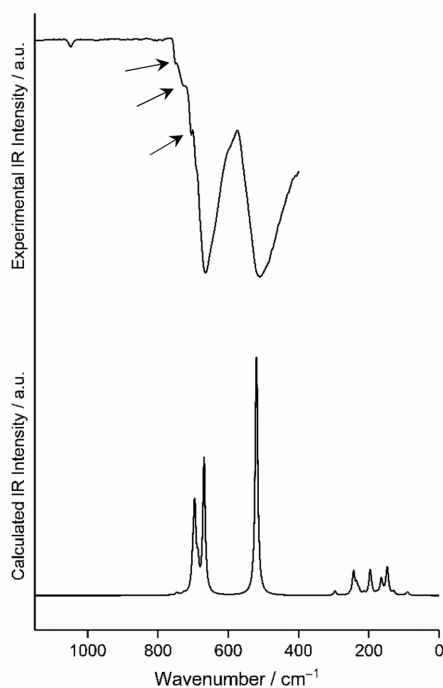


Figure 4. Experimental (above) and calculated (below) IR spectrum of WF_5 . Arrows point to low-intensity shoulders.

ected by powder X-ray diffraction and a common by-product of the reaction.^[23] The IR spectrum was also studied with solid-state quantum-chemical calculations (CRYSTAL17, DFT-PBE0).^[24,25] This calculated IR spectrum correlates quite well with the recorded one; both are reported in Figure 4.

The band arising at 510 cm^{-1} in the IR spectrum of WF_5 is assigned to the asymmetric $\text{W}-\mu\text{-F}$ stretching mode. The remaining bands belonging to WF_5 are assigned to various symmetric and asymmetric $\text{W}-\text{F}_t$ stretching modes. The IR spectrum recorded for WF_5 in this work agrees well with the previously reported IR spectra for WF_5 .^[6] Moreover, the band locations and assignments observed in this work agree well with previously reported band wavenumbers and assignments for MoF_5 .^[21] A comparison of IR-active bands for the pentafluorides belonging to the MoF_5 structure type is given in Table 5.

Table 5. A comparison of the infrared-active bands observed for solid WF_5 , MoF_5 , NbF_5 , and TaF_5 . Abbreviations: s = strong, m = medium, w = weak, v = very, sh = shoulder. When given, a description of the vibrational modes are as follows: ν = stretching, ν_s = symmetric stretching, ν_{as} = asymmetric stretching. $\mu\text{-F}$ refers to bridging fluorine atoms and F_t refers to terminal fluorine atoms. All band positions are given in cm^{-1} .

WF_5 (this work)	WF_5 ^[6]	MoF_5 ^[21]	NbF_5 ^[26]	TaF_5 ^[22]
510s, $\nu_{as}(\text{W}-\mu\text{-F})$;	520m	496s	479w 514ms 661m	512m 579s
664s, $\nu(\text{W}-\text{F}_t)$	680vs	675s	688s	601vw
706sh, $\nu_s(\text{W}-\text{F}_t)$		720sh		667vw
727sh, $\nu_{as}(\text{W}-\text{F}_t)$	730vs	739sh	734vs	723w
751sh, $\nu_s(\text{W}-\text{F}_t)$	760vs	762sh		753m
1048vw ^{a)}				

a) Band belonging to WOF_4 .

Conclusions

Tungsten pentafluoride was synthesized for the first time by a photochemical reduction of WF_6 utilizing H_2 as a reductant and Hg as a photosensitizer. The single-crystal X-ray structure of WF_5 was obtained which verified that WF_5 crystallizes in the MoF_5 structure type, as predicted by Edwards,^[3] and gave precise atomic coordinates. A powder X-ray diffraction pattern obtained on a poly-crystalline sample of WF_5 confirmed the lattice parameters determined by single-crystal diffraction for WF_5 and showed that the compound can be obtained in a phase-pure form.^[3] An IR spectrum of WF_5 showed it to have similar band positions and assignments as MoF_5 , NbF_5 , and TaF_5 and proved the absence of HF or moisture.^[6,21,27,28] However, a very small amount of WOF_4 was observed in the IR spectrum.

Experimental Section

General Procedures and Materials: All operations were performed in either stainless steel (316L) or Monel metal vacuum lines, which were passivated with undiluted fluorine at various pressures before use. Preparations were carried out in an atmosphere of dry and purified argon (5.0, Praxair). Tungsten hexafluoride (99%, ABCR) and mercury were distilled once prior to use. Perfluorinated ethylene propylene polymer, FEP, was used to fabricate reaction vessels.

Synthesis of WF_5 : To synthesize WF_5 , 0.23 g (1.2 mmol) of Hg was added to an FEP reaction vessel (45 mL) and 0.96 g of WF_6 (3.2 mmol) was distilled into it followed by the addition of 950 mbar of H_2 (1.8 mmol) at -196°C . The reaction mixture was slowly warmed to room temperature and then irradiated with UV light (low-pressure Hg lamp OSRAM Puritec HNS S 11 W G23, main line 254 nm) in a homemade UV reactor for approximately 15 h (CAUTION: care should be taken to ensure the sample does not overheat during irradiation). Irradiation resulted in a brown-yellow sample that contained yellow single-crystals of WF_5 . The volatile species were removed in vacuo and the WF_5 was collected under an inert atmosphere in a glovebox. The yield of WF_5 was calculated to be approximately 70%, although it is suspected that WF_4 and WOF_4 were present as impurities (the latter presumably arose from the diffusion of H_2O through the FEP reaction vessel walls). If this synthesis was to be used for further syntheses involving WF_5 , it is strongly recommended that the WF_5 be sublimed at least once before use.

Single-Crystal X-ray Diffraction: The single-crystal X-ray structure determination of WF_5 was carried out with a STOE IPDS 2T dif-

fractometer with plane graphite-monochromated molybdenum radiation ($\text{Mo-}K_{\alpha}$, $\lambda = 0.71073 \text{ \AA}$) generated by a sealed X-ray tube ($12 \times 0.4 \text{ mm}$ long fine focus), and a detector resolution of $6.67 \text{ pixels mm}^{-1}$. Evaluation and integration of the diffraction data was carried out using the X-Area software, and absorption corrections were made through integration using the X-Red32 and X-Shape program within the parent software.^[29] The structure was solved using Direct Methods (SHELXT 2014/5) and refined against F^2 (SHELXL-2018/3).^[30,31] Representations of the crystal structure were created using the Diamond software.^[32]

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1993856 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Powder X-ray Diffraction: A Powder X-ray diffraction pattern was obtained with a Stadi-MP-Diffractometer (STOE) using $\text{Cu-}K_{\alpha 1}$ radiation ($\lambda = 1.5406 \text{ \AA}$), a germanium monochromator, and a Mythen1K detector. The data were handled using the WINXPow software.^[33] A poly-crystalline sample of WF_5 was filled into borosilicate capillaries, which were previously flamed dried under vacuum, and sealed using a hot tungsten wire under inert atmosphere in a glovebox.

IR Spectroscopy: The IR spectrum was measured on an alpha FTIR spectrometer (Bruker) using a diamond ATR unit in an argon atmosphere. The spectrum was processed with the OPUS software package.^[34]

Computational Details: Periodic quantum chemical calculations were carried out for the solid-state structure of WF_5 using the PBE0 density functional method (DFT-PBE0).^[24,25] A triple-zeta-valence + polarization (TZVP) level basis set was applied for W and split-valence + polarization (SVP) level basis set was applied for F.^[35,36] All calculations were carried out using the CRYSTAL17 program package.^[37] The reciprocal space was sampled using a $3 \times 3 \times 5$ Monkhorst-Pack-type k-point grid. For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, and 16 were used for all calculations. Both the atomic positions and lattice constants were fully optimized within the constraints imposed by the space group symmetry. Default optimization convergence thresholds were applied in all calculations. The optimized lattice parameters and atomic positions are given in the Supporting Information.

The harmonic vibrational frequencies and IR intensities were obtained through usage of the computational scheme implemented in CRYSTAL17.^[38–41] For the IR spectrum, a Lorentzian lineshape and an FWHM of 8 cm^{-1} was used. The band assignments were carried out by visual inspection of the normal modes using the Jmol program package.^[42]

Supporting Information (see footnote on the first page of this article): The supporting information contains the optimized structure of tungsten pentafluoride from quantum-chemical solid-state calculations.

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Keywords: Fluorides; Tungsten; Photoreaction; IR spectroscopy; Single-crystal X-ray diffraction

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Photochemical Synthesis of Tungsten Pentafluoride, WF_5

