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Photochemical Synthesis of Tungsten Pentafluoride, WF₅

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

Abstract. A new synthetic route for the synthesis of WF₅ utilizing a mercury photosensitized reduction of tungsten hexafluoride with H₂ is described. Crystals of WF₅ were studied using single-crystal X-ray diffraction, resulting in the first-reported crystal structure of WF₅. Powder X-ray diffraction studied at room-temperature showed the compound was phase-pure. The IR spectrum of WF₅ 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 WOF₄, that were only observed in the IR spectrum.

Introduction

Studies describing the synthesis and characterization of tungsten pentfluoride (WF₅) 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 WF₅ 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 WF₅.[1,2] To perform this synthesis, NaWF₆ was dissolved in anhydrous hydrogen fluoride (aHF) and to this solution a quantity of SbF₅ was applied for the synthesis of WF₅(NC₅H₅)₂. Unfortunately, our initial studies into this reaction were unsuccessful because the reaction described by Equation (1) does not proceed:

2 WF₆ + H₂ → 2 WF₅ + 2 HF

(1)

This result is not surprising because WF₆ 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 (1S₀ ground state) is irradiated with 254 nm light, excited atoms of Hg (2P₁, 3P₂) are formed having an excitation energy of 112 kcal mol⁻¹.[12] When H₂ is present, the H⁺ 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 WF₅ may be produced by means of the following reaction, Equation (2):

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2WF₆ + H₂ ——> 2WF₅ + 2HF

More details regarding this reaction will be discussed below.

Herein we report upon a new synthetic method for the synthesis of WF₅ using photosensitization. Single-crystal X-ray diffraction leads to the first crystal structure determination of WF₅. 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 WF₅.

Results and Discussion

Synthesis of WF₅

To synthesize WF₅, a drop of mercury was added into a perfluorooctene/perfluoropropylene copolymer (FEP) reaction vessel and WF₆ was condensed into the reaction vessel followed by H₂ 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 WF₅. The volatile species were removed and the WF₅ 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 WF₆ to produce WF₅. Alternatively, although to a much smaller extent, the Hg* atoms may react directly with WF₆ to form WF₅ and a fluorine radical, according to Equation (3), Equation (4), Equation (5), Equation (6), Equation (7), and Equation (8).

2WF₆ + H₂ ——> 2WF₅ + 2HF

This photosensitization reaction seems dependent on the presence of H₂, because the reaction does not take place to any appreciable extent under other gaseous atmospheres, such as CO or CO₂.

Single-Crystal and Powder X-ray Diffraction

As predicted by Edwards,[13] WF₅ crystallizes in the MoF₅ structure type (mS48, j3i3h), space group C2/m (no. 12) with the lattice parameters of a = 9.4964(9), b = 14.1820(12), c = 5.0712(5) Å, β = 96.778(7)°, V = 678.21(11) Å³, Z = 8, T = 100 K. The crystal structure of the compound is characterized by W₄F₂₀ molecules formed from tetramerization of WF₅ units (see Figure 1). These molecules may be described by the Niggli formula ½[WF₂/F₂/F₄/F₄/F₄/F₄/F₄/F₄], that is, each tungsten atom has four terminally bound F atoms and two μ₂-bridging F atoms. Atomic coordinates and equivalent isotropic displacement parameters for WF₅ are reported in Table 1; selected crystallographic data and details of the single-crystal structure determination are given in Table 2.

Additionally, a powder X-ray diffraction pattern of WF₅ 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, β = 94.5598(4)°, 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 Uₐₐ at 100 K for WF₅ obtained from single-crystal X-ray diffraction.

| Atom | Position | x   | y   | z   | Uₐₐ /Å² |
|------|----------|-----|-----|-----|---------|
| 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) | 0.0119(11) |
| F(2) | 4i       | 0.1629(6) | ½ | 0.4062(11) | 0.0119(12) |
| F(3) | 8j       | 0.1276(4) | 0.4059(3) | 0.8605(8) | 0.0185(9) |
| F(4) | 8j       | 0.3737(4) | 0.6093(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) | 0.3799(9) | 0.0177(9) |

Figure 1. The W₄F₂₀ tetramer observed in the solid-state structure of WF₅. 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.

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

|            | WF₅ (SCXRD) at 100 K | WF₅ (PXRD) at 298 K |
|------------|----------------------|----------------------|
| Empirical formula | F₅W                 | F₅W                  |
| 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                |                      |
| a /Å               | 9.4964(9)           | 9.6431(7)            |
| b /Å               | 14.1820(12)         | 14.32135(10)         |
| c /Å               | 5.0712(5)           | 5.24942(4)           |
| β /°               | 96.778(7)           | 94.5598(4)           |
| V /Å³              | 678.21(11)          | 722.753(9)           |
| Z                  | 8                   |                      |
| σ /g·cm⁻³          | 5.462               | 5.125                |
| λ /Å               | 0.71073 (Mo-Kα)     | 1.5406 (Cu-Kα₁)      |
| T /K               | 100                 | 293                  |
| μ /mm⁻¹            | 34.040              | 59.478               |
| θmin /°            | 2.873               | –                    |
| θmax /°            | 31.497              | –                    |
| 2θ range measured /° | –                   | 10.00–94.96          |
| 2θ range refined /° | –                   | 10.00–94.96          |
| hkl range          | –13 ≤ h ≤ 12; −20 ≤ k ≤ 20; −7 ≤ l ≤ 7 | – |
| Rint, Rσ           | 0.075, 0.039        | –                    |
| R(F) [I ≥ 2σ(I), all data] | 0.028, 0.033     | –                    |
| wR(F²) [I ≥ 2σ(I), all data] | 0.067, 0.070   | –                    |
| Rp, wRp            | –                   | 0.027, 0.038         |
| cRp, cwRp a)       | –                   | 0.141, 0.121         |
| R(Bragg(I))        | –                   | 0.021                |
| S (all data)       | 1.05                | 2.62                 |
| Data, parameter, restraints | 1171, 61, 0 | 5665, 96, 5 b) |
| Δρmax, Δρmin /e·Å⁻³ | 2.31, −2.07        | –                    |

a) Background-corrected R-factors. b) Uiso 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. 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, $β = 94.6°$. 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 isotypic pentafluorides, MoF$_5$, NbF$_5$, and TaF$_5$.

| Atom1  | Atom2  | d /Å (WF$_5$) | d /Å (MoF$_5$) | d /Å (MoF$_5$) | d /Å (NbF$_5$) | d /Å (TaF$_5$) |
|--------|--------|---------------|----------------|---------------|----------------|---------------|
| M(1)   | M(1)'  | 5.7922(6)     | 5.7776(5)      | 5.800(6)      | 5.800(6)       | –             |
| M(2)   | M(2)'  | 5.8099(7)     | 5.7853(5)      | 5.860(6)      | 5.900(6)       | –             |
| M(1)   | M(2)   | 4.0988(4)     | 4.0881(3)      | 1.82(9)       | 1.78(5)       | 1.858(10)     |
| M(1)   | F(5)   | 1.824(4)      | 1.8012(13)     | 1.89(4)       | 1.75(2)       | 1.840(11)     |
| M(1)   | F(6)   | 1.846(4)      | 1.8236(14)     | 2.04(4)       | 2.06(2)       | 2.073(8)      |
| M(1)   | μ-F(4) | 2.048(4)      | 2.0243(11)     | 2.04(4)       | 2.07(2)       | 2.058(8)      |
| M(2)   | μ-F(4) | 2.052(4)      | 2.0463(11)     | 2.09(4)       | –             | –             |
| M(2)   | F(1)   | 1.822(5)      | 1.8013(18)     | 1.69(10)      | 1.75(5)       | 1.852(15)     |
| M(2)   | F(2)   | 1.822(5)      | 1.8011(18)     | 1.66(10)      | 1.78(5)       | 1.881(15)     |
| M(2)   | F(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 isotypic pentafluorides, MoF$_5$, NbF$_5$, and TaF$_5$.

| Angle ° (WF$_5$) | Angle ° (MoF$_5$) | Angle ° (MoF$_5$) | Angle ° (NbF$_5$) | Angle ° (TaF$_5$) |
|------------------|------------------|------------------|------------------|------------------|
| M(1)–μ-F(4)–M(2) | 178.1(2)         | 178.20(7)        | 180.0(20)        | 182.5(20)        | 172.9(5)        |
| Ft(5)–M(1)–Ft(5) | 163.9(3)         | 162.23(10)       | 165.8(25)        | 164.0(25)        | 164.1(7)        |
| Ft(6)–M(1)–μ-F(4) | 177.76(19)       | 178.04(6)        | –                | 172.7(5)        |
| Ft(1)–M(2)–F(2)  | 163.2(3)         | 161.74(9)        | 164.7(30)        | 167.0(25)       | 161.9(6)        |
| Ft(3)–M(2)–μ-F(4) | 177.75(17)       | 178.15(6)        | –                | 172.7(4)        |

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.\cite{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.\cite{17–20} Additionally, within the MoF$_5$ structure type, the point symmetry of the $M_4F_{20}$ ($M = Nb, Ta, Mo, W$) 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 $M_4F_{20}$ ($M = Ru, Os, Rh, Pt$) molecule has $C_1$ 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, Ft, and two bridging fluorine atoms, μ-F) to form octahedron-like coordination polyhedra. The W–Ft distances range between 1.822(5) and 1.846(4) Å, and the W–μ-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. A comparison of selected atomic distances observed in these pentafluorides is reported in Table 3. 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 WF₅. Arrows point to low-intensity shoulders.

Conclusions

Tungsten pentfluoride was synthesized for the first time by a photochemical reduction of WF₆ utilizing H₂ as a reductant and Hg as a photosensitizer. The single-crystal X-ray structure of WF₅ was obtained which verified that WF₅ crystallizes in the MoF₅ 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 WF₅ confirmed the lattice parameters determined by single-crystal diffraction for WF₅ and showed that the compound can be obtained in a phase-pure form.[13] An IR spectrum of WF₅ showed it to have similar band positions and assignments as MoF₅, NbF₅, and TaF₅ and proved the absence of HF or moisture.[6,21,27,28] However, a very small amount of WOF₄ 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 WF₅: To synthesize WF₅, 0.23 g (1.2 mmol) of Hg was added to an FEP reaction vessel (45 mL) and 0.96 g of WF₆ (3.2 mmol) was distilled into it followed by the addition of 950 mbar of H₂ (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 WF₅. The volatile species were removed in vacuo and the WF₅ was collected under an inert atmosphere in a glovebox. The yield of WF₅ was calculated to be approximately 70%, although it is suspected that WF₄ and WOF₄ were present as impurities (the latter presumably arose from the diffusion of H₂O through the FEP reaction vessel walls). If this synthesis was to be used for further syntheses involving WF₅, it is strongly recommended that the WF₅ be sublimed at least once before use.

Single-Crystal X-ray Diffraction: The single-crystal X-ray structure determination of WF₅ was carried out with a STOE IPDS 2T diffractometer 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 WF₅ is assigned to the asymmetric W–μ-F stretching mode. The remaining bands belonging to WF₅ are assigned to various symmetric and asymmetric W–Fₜ stretching modes. The IR spectrum recorded for WF₅ in this work agrees well with the previously reported IR spectra for WF₅.[6] Moreover, the band locations and assignments observed in this work agree well with previously reported band wavenumbers and assignments for MoF₅.[21] A comparison of IR-active bands for the pentafluorides belonging to the MoF₅ structure type is given in Table 5.

| Band (cm⁻¹) | Assignment | WF₅[6]  | MoF₅[21] | NbF₅[26] | TaF₅[22] |
|------------|------------|--------|---------|---------|---------|
| 510s, νₚ(W–μ-F); | 520m | 496s | 479w | 512m |
| 664s, ν(W–Fₜ) | 680vs | 675s | 688s | 601wv |
| 706sh, νₚ(W–Fₜ) | 720sh | 739sh | 734vs | 723w |
| 751sh, νₚ(W–Fₜ) | 762vs | 762sh | 753m |

Table 5. A comparison of the infrared-active bands observed for solid WF₅, MoF₅, NbF₅, and TaF₅. Abbreviations: s = strong, m = medium, w = weak, v = very, sh = shoulder. When given, a description of the vibrational modes are as follows: ν = stretching, νₛ = symmetric stretching, νₚ = asymmetric stretching. μ-F refers to bridging fluorine atoms and Fₜ refers to terminal fluorine atoms. All band positions are given in cm⁻¹.

a) Band belonging to WOF₄.
fractometer with plane graphite-monochromated molybdenum radiat-
ion (Mo-Kα, λ = 0.71073 Å) generated by a sealed X-ray tube
(12 × 0.4 mm long fine focus), and a detector resolution of 6.67 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 F² (SHELXL-2018/3).[10,31]
Representations of the crystal structure were created using the Dia-
mond 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 de-
pository 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 Cu-
Kα (λ = 1.5406 Å), a germanium monochromator, and a Mythen1K
detector. The data were handled using the WINXPOW software.[13] A
poly-crystalline sample of WF₅ was filled into borosilicate capillaries,
which were previously flame-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 atmo-
sphere. The spectrum was processed with the OPUS software pack-
age.[14]

Computational Details: Periodic quantum chemical calculations were
carried out for the solid-state structure of WF₅ using the PBE0 density
functional method (DFT-PBE0).[24,25] A triple-zeta-valence + polariza-
tion (TZVP) level basis set was applied for W and split-valence +
SVP level basis set was applied for F.[35,36] All calcula-
tions were carried out using the CRYSTAL17 program package.[37]
Periodic quantum chemical calculations were

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
a FWHM of 8 cm⁻¹ was used. The band assignments were carried
out by visual inspection of the normal modes using the Jmol program
c-package.[42]

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

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troscopy; Single-crystal X-ray diffraction

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Photochemical Synthesis of Tungsten Pentafluoride, WF₅