

Redetermination of the crystal structure of NbF₄

Jascha Bandemehr, Matthias Conrad and Florian Kraus*

Anorganische Chemie, Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-Strasse 4, 35032 Marburg, Germany. *Correspondence e-mail: florian.kraus@chemie.uni-marburg.de

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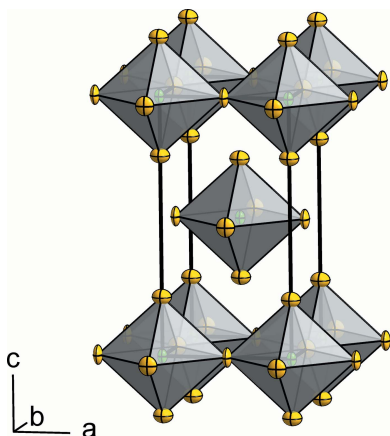
Single crystals of NbF₄, niobium(IV) tetrafluoride, were synthesized by disproportionation of Nb₂F₅ at 1273 K in a sealed niobium tube, extracted and studied by single-crystal X-ray diffraction. Previous reports on the crystal structure of NbF₄ were based on X-ray powder diffraction data and the observed isotypicity to SnF₄ [Gortsema & Didchenko (1965). *Inorg. Chem.* **4**, 182–186; Schäfer *et al.* (1965). *J. Less Common Met.* **9**, 95–104]. The data obtained from a single-crystal X-ray diffraction study meant the atomic coordinates could now be refined as well as their anisotropic displacement parameters, leading to a significant improvement of the structural model of NbF₄. In the structure, the Nb atom is octahedron-like surrounded by six F atoms of which four are bridging to other NbF₆ octahedra, leading to a layer structure extending parallel to the *ab* plane.

1. Chemical context

The first synthesis of niobium tetrafluoride was reported by Schäfer and co-workers by reduction of niobium pentafluoride with niobium metal (Schäfer *et al.*, 1964). According to Gortsema and coworker, a reduction of NbF₅ with silicon is seemingly the best way to obtain pure NbF₄ (Gortsema & Didchenko, 1965). The obtained products were reported as dark-blue or black powders, respectively (Gortsema & Didchenko, 1965, Schäfer *et al.*, 1964). However, we obtained green NbF₄ single crystals among a green powder. NbF₄ is moisture sensitive and deliquesces to a brown suspension. In aqueous medium a brown precipitate is formed. It is reported to be soluble in hydrochloric acid, sulfuric acid or hydrogen fluoride (Schäfer *et al.*, 1965). The compound disproportionates under vacuum above 623 K to NbF₅ and a fluoride of which the compositions were reported as NbF_{2.37} (Schäfer *et al.*, 1965) or NbF₃ (Gortsema & Didchenko, 1965). In a sealed niobium ampoule NbF₄ disproportionates at 825 K to NbF₅ and Nb₂F₅ (Chassaing & Bizot, 1980). Infrared spectra (Dickson, 1969), UV/Vis-spectra (Chassaing & Bizot, 1980) and powder X-ray patterns are available for NbF₄ (Gortsema & Didchenko, 1965, Schäfer *et al.*, 1965). Magnetic measurements show that NbF₄ orders antiferromagnetic in contrast to the other niobium tetrahalides which are reported to be diamagnetic (Chassaing & Bizot, 1980).

2. Structural commentary

The lattice parameters obtained by our single-crystal structure determination of *a* = 4.0876 (5), *c* = 8.1351 (19) Å are in good agreement with those obtained previously from powder X-ray diffraction data recorded on film (*a* = 4.081, *c* = 8.162 Å;



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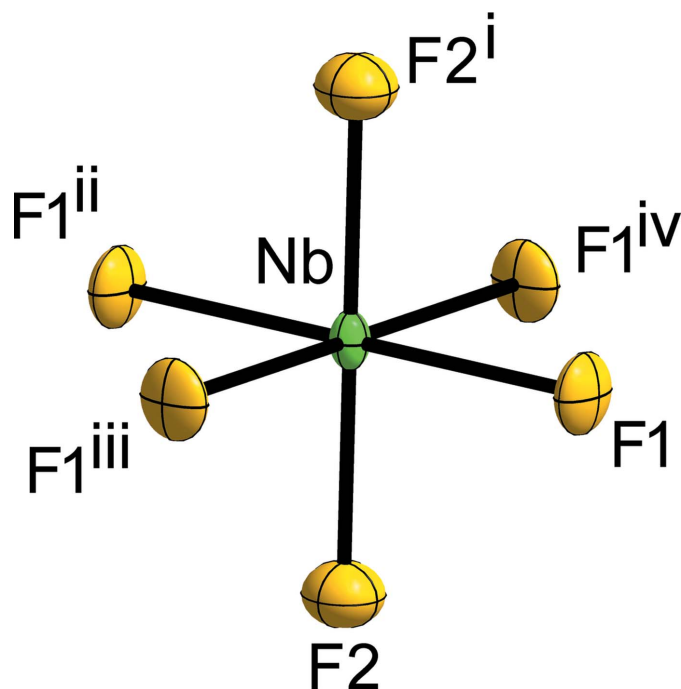


Figure 1

A section of the crystal structure of the title compound displaying the coordination polyhedron around the Nb atom. Displacement ellipsoids are shown at the 70% probability level at 293 K. [Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y - 1, z$; (iii) $-y, x, z$; (iv) $-y + 1, x, z$.]

Gortsema & Didchenko, 1965; $a = 4.08$ (3), $c = 8.16$ (1) Å; Schäfer *et al.*, 1965).

NbF_4 crystallizes in the SnF_4 structure type (Hoppe & Dähne, 1962; Bork & Hoppe, 1996), which has been discussed extensively and its structural relationship to the NaCl structure type (Müller, 2013) deduced. The Nb atom resides on Wyckoff position $2a$ (site symmetry $4/mmm$) and is octahedron-like coordinated by six fluorine atoms of which four are bridging to further octahedra, thus corner-sharing connections are obtained. These Nb–(μ -F) distances, with the F1 atoms residing on the $4c$ (mmm) position, are observed to be 2.0438 (3) Å and the Nb–F–Nb angle is 180° due to space-group symmetry. The structure models based on powder diffraction data yielded 2.041 (Gortsema & Didchenko, 1965) and 2.042 Å (Schäfer *et al.*, 1965) for these Nb–F distances. The Nb–(μ -F) distance is similar to the respective ones of NbF_5 [2.06 (2) and 2.07 (2) Å; Edwards, 1964] but shorter than the respective one of Nb_2F_5 [2.1179 (4) Å; Knoll *et al.*, 2006]. Two fluorine atoms (F2, $4e$, $4mm$) of the title compound are not bridging and are *trans* arranged at the Nb atom. As expected, the non-bridging F2 atoms show shorter Nb–F distances of 1.8524 (19) Å; these values differ significantly from those of 2.0405 (Gortsema & Didchenko, 1965) and 2.040 Å (Schäfer *et al.*, 1965). The F2 atoms are surrounded by twelve F atoms (eight symmetry-equivalent F1 and four F2 atoms) in the shape of a distorted cuboctahedron. A ‘central’ F2 atom is displaced by 0.24 Å from the center of this cuboctahedron towards the Nb atom to which it is bound. Hence the expected deviation from $m\bar{3}m$ (O_h) to $4/mmm$ (D_{4h}) symmetry is much more obvious. In comparison to the Nb–F

distances (non-bridging F-atoms) of NbF_5 , which are reported to be 1.75 (5) and 1.78 (5) Å (Edwards, 1964), an elongation is observed. This is attributed to the higher oxidation state of the Nb atom in NbF_5 . Fig. 1 shows a section of the crystal structure displaying the coordination polyhedron around the Nb atom. As in SnF_4 , infinite layers with Niggli formula $\infty^2[\text{NbF}_{4/2}\text{F}_{2/1}]$ are present and extend parallel to the ab plane. The crystal structure is shown in Fig. 2.

3. Synthesis and crystallization

Niobium tetrafluoride was synthesized by heating brown Nb_2F_5 (54.4 mg, 0.16 mmol) to 1273 K in a sealed niobium tube (22 mm, 4 mm i.d., 6 mm o.d.) which was placed upright in an evacuated sealed silica tube. The heating rate was 20 K h^{-1} and the maximum temperature was held for two days. The niobium ampoule had been charged under nitrogen atmosphere in a glove box and sealed by arc welding. Nb_2F_5 was also synthesized in a niobium ampoule (33 mm, 4 mm i.d., 6 mm o.d.) starting from niobium metal and niobium pentafluoride with a heating rate of 16 K h^{-1} . The maximum temperature of 1073 K was held for two days. The ampoules were allowed to cool to room temperature and were opened under inert atmosphere. A powder X-ray diffraction pattern of the green product shows the reflections of NbF_4 , Nb and an yet unidentified phase. It seems that Nb_2F_5 disproportionates to NbF_5 and Nb, and by cooling NbF_4 is formed. This assumption is supported by the observation that high pressure

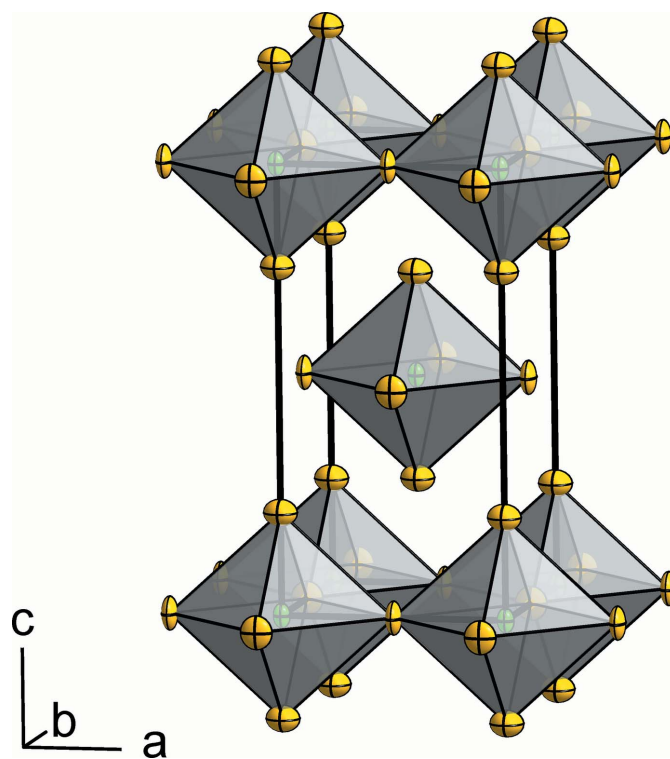


Figure 2

The crystal structure of NbF_4 presented as a polyhedron model. Displacement ellipsoids are shown at 70% probability level at 293 K.

inside the ampoule blew it up. The pressure is likely induced by gaseous NbF₅, and the disproportionation of Nb₂F₅ to Nb and NbF₅ is known from the literature (Schäfer *et al.*, 1965). A selected single crystal of NbF₄ was investigated using X-ray diffraction and diffraction data measured at room temperature.

4. Refinement

As a starting model for the structure refinement, the atomic coordinates of the SnF₄ structure type were used. Crystal data, data collection and structure refinement details are summarized in Table 1. One reflection (112) was omitted from the refinement as it was affected by the primary beam stop.

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Table 1
Experimental details.

Crystal data	
Chemical formula	NbF ₄
<i>M_r</i>	168.91
Crystal system, space group	Tetragonal, <i>I4/mmm</i>
Temperature (K)	293
<i>a</i> , <i>c</i> (Å)	4.0876 (5), 8.1351 (19)
<i>V</i> (Å ³)	135.93 (5)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	4.32
Crystal size (mm)	0.06 × 0.04 × 0.01
Data collection	
Diffractometer	Stoe IPDS 2T
Absorption correction	Integration (<i>X-RED32</i> and <i>X-SHAPE</i> ; Stoe & Cie, 2009)
<i>T_{min}</i> , <i>T_{max}</i>	0.664, 0.925
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	1392, 167, 167
<i>R_{int}</i>	0.057
(sin θ/λ) _{max} (Å ⁻¹)	0.944
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.014, 0.032, 0.98
No. of reflections	167
No. of parameters	10
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.69, −0.58

Computer programs: *X-AREA* (Stoe & Cie, 2011), *X-RED32* (Stoe & Cie, 2009), *SHELXL2014* (Sheldrick, 2015) and *DIAMOND* (Brandenburg, 2015).

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Computing details

Data collection: *X-AREA* (Stoe & Cie, 2011); cell refinement: *X-AREA* (Stoe & Cie, 2011); data reduction: *X-RED32* (Stoe & Cie, 2009); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 2015); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

Niobium(IV) tetrafluoride

Crystal data

NbF ₄	$D_x = 4.127 \text{ Mg m}^{-3}$
$M_r = 168.91$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Tetragonal, $I4/mmm$	Cell parameters from 2534 reflections
$a = 4.0876 (5) \text{ \AA}$	$\theta = 5.0\text{--}42.2^\circ$
$c = 8.1351 (19) \text{ \AA}$	$\mu = 4.32 \text{ mm}^{-1}$
$V = 135.93 (5) \text{ \AA}^3$	$T = 293 \text{ K}$
$Z = 2$	Plate, green
$F(000) = 154$	$0.06 \times 0.04 \times 0.01 \text{ mm}$

Data collection

Stoe IPDS 2T	$T_{\min} = 0.664, T_{\max} = 0.925$
diffractometer	1392 measured reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	167 independent reflections
Plane graphite monochromator	167 reflections with $I > 2\sigma(I)$
Detector resolution: 6.67 pixels mm^{-1}	$R_{\text{int}} = 0.057$
rotation method scans	$\theta_{\max} = 42.1^\circ, \theta_{\min} = 5.0^\circ$
Absorption correction: integration	$h = -7 \rightarrow 5$
(<i>X-RED32</i> and <i>X-SHAPE</i> ; Stoe & Cie, 2009)	$k = -7 \rightarrow 7$
	$l = -14 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: isomorphous structure methods
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.025P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.014$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.032$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 0.98$	$\Delta\rho_{\max} = 0.69 \text{ e \AA}^{-3}$
167 reflections	$\Delta\rho_{\min} = -0.58 \text{ e \AA}^{-3}$
10 parameters	Extinction correction: SHELXL2014 (Sheldrick, 2015),
0 restraints	$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Primary atom site location: isomorphous structure methods	Extinction coefficient: 0.026 (5)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Nb	0.0000	0.0000	0.0000	0.00798 (9)
F1	0.0000	0.5000	0.0000	0.0167 (3)
F2	0.0000	0.0000	0.2277 (2)	0.0209 (3)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Nb	0.00583 (10)	0.00583 (10)	0.01230 (11)	0.000	0.000	0.000
F1	0.0211 (7)	0.0056 (5)	0.0235 (6)	0.000	0.000	0.000
F2	0.0239 (5)	0.0239 (5)	0.0149 (5)	0.000	0.000	0.000

Geometric parameters (\AA , $^\circ$)

Nb—F2 ⁱ	1.8524 (19)	Nb—F1 ⁱⁱⁱ	2.0438 (3)
Nb—F2	1.8524 (19)	Nb—F1 ^{iv}	2.0438 (3)
Nb—F1	2.0438 (3)	F1—Nb ^v	2.0438 (3)
Nb—F1 ⁱⁱ	2.0438 (3)		
F2 ⁱ —Nb—F2	180.0	F1—Nb—F1 ⁱⁱⁱ	90.0
F2 ⁱ —Nb—F1	90.0	F1 ⁱⁱ —Nb—F1 ⁱⁱⁱ	90.0
F2—Nb—F1	90.0	F2 ⁱ —Nb—F1 ^{iv}	90.0
F2 ⁱ —Nb—F1 ⁱⁱ	90.0	F2—Nb—F1 ^{iv}	90.0
F2—Nb—F1 ⁱⁱ	90.0	F1—Nb—F1 ^{iv}	90.0
F1—Nb—F1 ⁱⁱ	180.0	F1 ⁱⁱ —Nb—F1 ^{iv}	90.0
F2 ⁱ —Nb—F1 ⁱⁱⁱ	90.0	F1 ⁱⁱⁱ —Nb—F1 ^{iv}	180.0
F2—Nb—F1 ⁱⁱⁱ	90.0	Nb ^v —F1—Nb	180.0

Symmetry codes: (i) $-x, -y, -z$; (ii) $x, y-1, z$; (iii) $-y, x, z$; (iv) $-y+1, x, z$; (v) $x, y+1, z$.