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$NOUF_6$ revisited. A comprehensive study of a hexafluoridouranate(V) salt.

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Abstract: We have synthesized $NOUF_6$ by direct reaction of NO with UF_6 in anhydrous HF. Based on the unit cell volume and powder diffraction data, the compound was previously reported to be isotypic to O_2PtF_6, however detailed structural data, such as the atom positions and all information that can be derived from those, were unavailable. We have therefore investigated the compound using single-crystal and powder X-ray diffraction, IR, Raman, NMR, EPR, photoluminescence spectroscopy and magnetic measurements, as well as chemical analysis, density determination and quantum chemical calculations.

Introduction

The ionic compound nitrosyl hexafluoridouranate(V), $NOUF_6$, was probably first synthesized in the laboratories of the Oak Ridge Gaseous Diffusion Plant.[1] It was then further characterized at the Goodyear Atomic Corporation and Brookhaven National Laboratory, at the latter one in the course of reprocessing nuclear fuel elements.[1–3] For the separation of uranium isotopes the chemical exchange reaction with UF_6, in the gas phase and in liquid systems, was studied, as seen in Equation 1.[4–7]

$$ {}^{238}UF_6 + NO^{235}UF_6 \rightleftharpoons {}^{235}UF_6 + NO^{238}UF_6 \qquad (1)$$

Until now several preparation methods for $NOUF_6$ were described, such as the oxidation of uranium metal or uranium carbide in violet hydrogen fluoride, a NO_x/HF mixture which is a potent oxidant, or the reduction of uranium hexafluoride with nitric oxide, NO.[3,8–13] UF_6 thus shows the same reaction behavior as most of the other metal hexafluorides, MF_6, which are capable to oxidize NO, under formation of nitrosyl hexafluoridometallates(V), as shown in Equation 2.[10,13,14]

$$\begin{gathered} MF_6 + NO \longrightarrow NOMF_6 \\ M = \mathrm{Mo, Tc, Re, Os, Ir, Pt, U, Pu} \end{gathered} \qquad (2)$$

Some chemistry of $NOUF_6$ is known.[15,16] For example, there has been a description of metathesis reactions between alkali metal nitrates, $M\,NO_3$, and $NOUF_6$ under liberation of nitrogen dioxide, in order to obtain alkali metal hexafluoridouranates(V), $M\,UF_6$, according to Equation 3.[15]

$$\begin{gathered} MNO_3 + NOUF_6 \xrightarrow{\Delta T} MUF_6 + 2\ NO_2 \\ M = \mathrm{Li - Cs} \end{gathered} \qquad (3)$$

Other methods to prepare hexafluoridouranate(V) salts are for example reactions of fluoride salts with uranium pentafluoride in anhydrous hydrogen fluoride, concentrated hydrofluoric acid or acetonitrile, as well as solid state reactions.[17–20] UF_6^- salts exhibit the $[Rn]5f^1$ electronic configuration, which is of interest for spectroscopic and theoretical studies, because of the absence of interelectronic repulsion within the f-orbitals.[21–23] Most of these compounds and other uranium(V) halides, UX_6^-, are covered in a review by Selbin and Ortego in 1969.[24] Probably the latest and most comprehensive overview exhibits the book "The Chemistry of the Actinide and Transactinide Elements", edited by Edelstein, Fuger and Morss.[25]

Here we report on the synthesis of $NOUF_6$, its single crystal structure as well as its further spectroscopic and physical properties, theoretical investigations, and compare them with available data for $NOUF_6$ and other UF_6^- salts.

Results and Discussion

The action of gaseous NO on a suspension of UF_6 in anhydrous HF at room temperature results in the formation of a white vapor and a yellowish HF solution. Upon cooling the reaction mixture

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with dry ice/isopropanol the HF turns blueish, which is characteristic for a HF solvated hexafluoridouranate(V) salt.[17] Slow evaporation of HF under cooling leads to the formation of blueish-green crystals of $NOUF_6$, see Equation 4. Those crystals are suitable for a single crystal structure determination.

Table ***1***). It is isotypic to O_2PtF_6, as before estimated from powder X-ray and neutron diffraction data.[13,26–28] The structure is related to the CsCl structure type via the space group *Pm*$\bar{3}$ (No. 200), see the Bärnighausen tree in

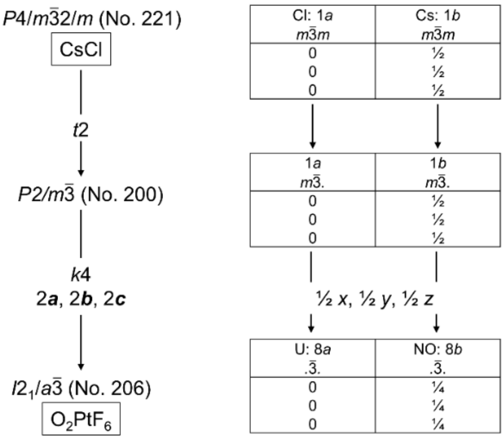

Figure ***1***.[29–31]

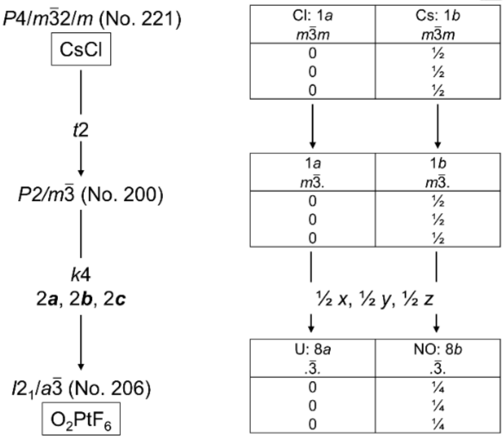

Figure 1. Structural relationship between the CsCl and O_2PtF_6 structure types. Note that the center in between the N and O atom is the 8*b* position.

A section of the crystal structure is shown in Figure 2. The uranium atom U(1) occupies the Wyckoff position 8*a* (site symmetry .$\bar{3}$.) and is coordinated by the fluorine atom F(1) to form the hexafluoridouranate(V) anion, as the other five fluorine atoms are generated by symmetry. The U−F distance is 2.0671(9) Å and the F−U−F angles are 180.00, 91.75(4) and 88.25(4)°,

$$UF_6 + NO \xrightarrow[-78^\circ C]{aHF} NOUF_6 \tag{4}$$

Single-crystal and powder X-ray structure analysis

$NOUF_6$ crystallizes in the cubic space group type *Ia*$\bar{3}$ (No. 206) with eight formula units in the unit cell (

respectively, forming a polyhedron close in shape to an octahedron. Those values agree with previously reported data for UF_6^- salts like $CsUF_6$, where the U−F distance is slightly shorter with 2.057(6) Å (*T* was not reported) and bis(triphenylphosphine)iminium hexafluoridouranate(V), $(PPN)UF_6$, with a mean U−F distance of 2.03(2) Å (*T* was not reported).[32,33] For $AgUF_6$ the reported structure is questionable, so it will not be discussed and merits further investigation.[34] Comparing the hexafluoridouranates(V) with *α*-UF_5, which also exhibits a six-fold coordination by fluorine atoms with a mean equatorial, non-bridging U−F distance of 2.020(5) Å (*T* was not reported), one can see a slight increase due to the negative charge.[35] In comparison to the mean U−F distance in UF_6 with 2.023(6) Å at 77 K, the distance in UF_6^- salts is also increased.[36] The nitrogen and oxygen atoms of the nitrosyl cation are observed to be disordered around the Wyckoff position 8*b* with symmetry .$\bar{3}$., both occupying the position 16*c*. The site occupation factor refines to 0.512(9), which is in nice agreement with the expected 50/50 occupancy. We note that we did not observe additional reflections in the powder or single crystal X-ray data that would indicate an ordering of the NO cation and thus a lowering of space group symmetry, which is in agreement with previous neutron diffraction studies at 4 K.[27,37] The N−O distance is 1.052(6) Å and agrees with the data reported for other nitrosyl salts like $NOXeOF_5$ (1.049(4) Å, *T* = 120 K) or $(NO)_2UF_8$ (mean N−O distance 1.024 Å, *T* = 120 K).[38,39] We derived an ordered model of $NOUF_6$ by decreasing the symmetry to the subgroup *I*2$_1$3 (No. 199) to enable quantum chemical calculations with density functional methods (DFT-PBE0, see experimental for computational details). In the ordered model, the number of symmetry operations decreases from 24 to 12 and the Wyckoff position 16*c*, occupied by N/O, splits into 8*a* + 8*a*, allowing ordered occupation of the N/O positions. Since there are two 8*a* positions, there are in principle two ways to distribute the N and O atoms, but a full structural optimization of both variants shows that the resulting structures are energetically equivalent and thus it does not matter which 8*a* site is N and which is O. This finding is also in line with the fact that the experimental structure shows ideal 50/50 occupancy of the 16c position in space group $Ia\bar{3}$. In the optimized structure, the UF_6^- anion with site symmetry S_6 ($\bar{3}$) shows three U–F distances of 2.049 Å and three U–F distances of 2.077 Å, resulting in a mean U–F distance of 2.063 Å. This compares very well with the experimental U–F distance of 2.0671(9) Å, as does also the N–O distance of 1.06 Å (exp. value 1.052(6) Å).

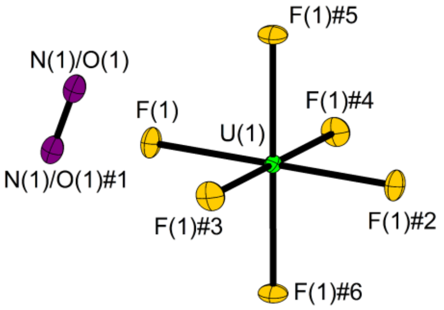

Figure 2. A section of the crystal structure of $NOUF_6$ showing the disordered NO^+ cation and the hexafluoridouranate(V) anion. Displacement ellipsoids are shown at the 70% probability level at 100 K. Symmetry transformations for the generation of equivalent atoms: #1 $-x + 1/2$, $-y + 3/2$, $-z + 3/2$; #2 $-x + 1$, $-y + 1$, $-z + 1$; #3 z, x, y; #4 $-z + 1$, $-x + 1$, $-y + 1$; #5 y, z, x; #6 $-y + 1$, $-z + 1$, $-x + 1$.

The crystal structure of $NOUF_6$ is made up of isolated UF_6^- units and disordered NO^+ cations (Figure 3). The barbell-like NO^+ cations point to the faces of the polyhedral. The U−U distance is 5.1740(2) Å, so no interaction of uranium(V) atoms can be inferred from the structure. Both the cations and anions are tilted alternately, and are coordinated eightfold by the respective counterion.

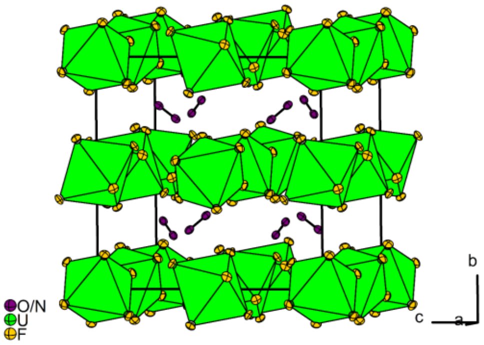

Figure 3. The crystal structure of $NOUF_6$. UF_6^- anions are shown as green polyhedra for the sake of clarity. Displacement ellipsoids are shown at the 70% probability level at 100 K.

The powder X-ray diffraction pattern of $NOUF_6$ recorded at room temperature (**Error! Reference source not found.**) could be indexed in the cubic crystal system with the unit cell parameters $a = 10.4631(2)$ Å, $V = 1145.47(4)$ Å^3, further details are given in

Table *1*. The first published powder X-ray data assigned a pseudo-cubic symmetry, with a nearly half as large lattice parameter (a = 5.179 Å, T not reported) than determined by Eller and coworkers (a = 10.4642(6) Å, T = 298 K), which are in nice agreement to our findings.[1,10,13,40]

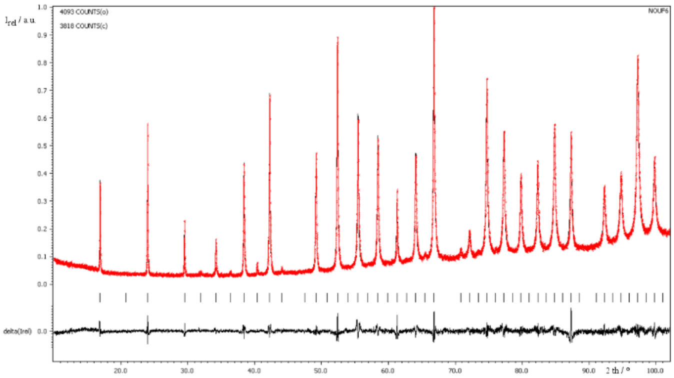

Figure 4. The powder X-ray diffraction pattern of cubic $NOUF_6$ with profile fitting. The strokes show the calculated reflection positions, the lower line plots the difference between the observed and calculated pattern. The compound was thus prepared phase-pure based on X-ray diffraction.

Table 1. Selected crystallographic data for $NOUF_6$.

	$NOUF_6$ (SCXRD)	$NOUF_6$ (PXRD)
Empirical formula	F_6NOU	
Color and appearance	blueish-green cubes	light green powder
Molecular mass / g·mol^{-1}	382.04	
Crystal system	cubic	
Space group (No.)	$Ia\bar{3}$ (206)	
a / Å	10.3480(3)	10.4631(2)
V / Å^3	1108.07(5)	1145.47(4)
Z	8	
$\rho_{calcd.}$ / g·cm^{-3}; $\rho_{exp.}$ / g·cm^{-3}	4.58; not det.	4.430; 4.4954(2)
λ / Å	0.71073 (Mo-K_α)	1.54051 (Cu-K_α)
T / K	100(2)	293
μ / mm^{-1}	29.356 (Mo-K_α)	86.645 (Cu-K_α)
θ_{max}	36.22	-
2θ range measured (min, max, increment)	-	10.00, 102.00, 0.015
2θ range refined (min, max)	-	10.00, 102.00
hkl_{max}	$-17 \le h \le 16$	-
	$-17 \le k \le 15$	-
	$-17 \le l \le 17$	-
Size / mm^3	0.09 · 0.13 · 0.17	-
R_{int}, R_σ	0.058, 0.023	-
$R(F)$ ($I \ge 2\sigma(I)$, all data)	0.017, 0.018	-
$wR(F^2)$ ($I \ge 2\sigma(I)$, all data)	0.050, 0.051	-
Rp, wRp	-	0.043, 0.057
S (all data)	1.31	-
Data, parameter, restraints	454, 17, 0	6134, 11, 0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e·Å^{-3}	1.46, −1.25	-

Vibrational spectroscopy

For an octahedral UF_6^- unit (O_h symmetry) one would expect three Raman ($\nu_1(A_{1g})$, $\nu_2(E_g)$, $\nu_5(F_{2g})$) and two IR active ($\nu_3(F_{1u})$, $\nu_4(F_{1u})$) normal modes, see Tables 2 and 3.[12,24,41] However, the site symmetry of the UF_6^- anion is only S_6 ($\bar{3}$), as observed from the single crystal X-ray structure. The $\nu_6(F_{2u})$ normal mode is inactive and thus can only be derived from combination modes or overtones.[27,42] The room temperature Raman and IR spectra are shown in Figure 5, values for $NOUF_6$ are listed in Tables 2 and 3, and for comparison the values of pure NO and UF_6 are given as well. We also calculated the Raman and IR spectra with the DFT-PBE0 method, and the calculated band positions are listed in Tables 2 and 3 (full spectral figures and assignments are available in the Supporting Information). The Raman spectrum shows three distinctive regions which are attributable to the UF_6^- ion. The totally symmetric U−F stretching mode ν_1 was assigned to the band at 612-618 cm^{-1}, a bathochromic shift of ~40 cm^{-1} in comparison to solid UF_6, consistent with the negative charge.[12,13,27] The doubly degenerate mode ν_2 splits into two separate bands at ~440 and ~490 cm^{-1}.[12,13,27] The triply degenerate F−U−F bending mode ν_5 splits into three distinctive bands, which we observed at 173, 203 and 225 cm^{-1}. In the previously reported data the assignment was ambiguous, e.g. Soulié assigned the split bands to impurities and others did not observe the third band of the ν_5 set.[12,13,27] From this splitting a lower symmetry than O_h can be derived, which is in accordance with our crystallographic data (site symmetry of U is $.\bar{3}.$). The splitting of the Raman modes is also confirmed by the predicted theoretical spectra and their full assignment (Supporting Information). A similar Raman spectrum has been observed for NO_2UF_6, thus the UF_6^- unit should exhibit also lower symmetry than O_h.[13] Concluding structural investigations are however not available for this compound, yet.

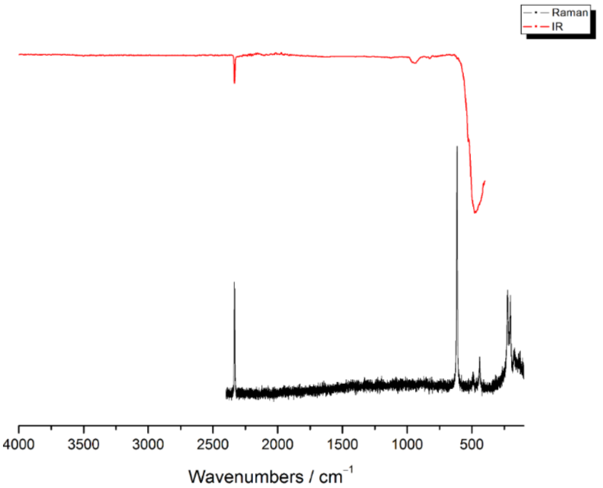

Figure 5. Room temperature IR (top) and Raman (bottom) spectra of solid $NOUF_6$.

In the IR spectrum a quite broad band at 479 cm^{-1} with a shoulder at 528 cm^{-1} can be observed. Those values are in accordance with previously reported ones, which were assigned to the ν_3 mode, thus also indicating lower symmetry than O_h.[10] The low intensity bands at ~950 cm^{-1} can be assigned to overtones of the split ν_3 band. The triply degenerate F−U−F bending mode ν_4 should lie in the far IR region, as may be derived from data on UF_6.[42] As expected, the split IR bending modes are present in the predicted DFT-PBE0 spectrum at wavenumbers 136, 148, and 175 cm^{-1}. Overall, the observed frequencies are in agreement with other UF_6^- salts.[24,25]

The ν(NO) stretching mode of the NO^+ cation was observed at ~2333 cm^{-1} both in the Raman and IR spectra. That is a hypsochromic shift of 467 cm^{-1} in comparison to gaseous NO, which is characteristic for NO^+ salts, as reported in the literature.[39,43–45]

Table 2. Raman active modes of NO, UF_6 and $NOUF_6$. All values in cm^{-1}.

Species	ν(NO)	$\nu_1(A_{1g})$ ν(U−F)	$\nu_2(E_g)$ ν(U−F)	$\nu_5(F_{2g})$ δ(F−U−F)	Reference
NO (g)	1876				[43]
UF_6 (s)		659	515	207, 219	[12]
$NOUF_6$ (s)	2234	615	440, 490	173, 203, 225	(exp.)
	2422	615	444, 485	167, 197, 225	(theory)
	~2330	618	441, 491	205, 228	[12]
	2333	612	437, 487	200, 221	[13]
		615	441, 495	166, 206, 225	[27]

Table 3. IR active modes of NO, UF_6 and $NOUF_6$. All values in cm^{-1}.

Species	ν(NO)	$\nu_3(F_{1u})$	$\nu_4(F_{1u})$	Reference

		ν(U−F)	δ(F−U−F)	
NO (g)	1876			[44]
UF_6 (g)		624	186	[42]
	2333	479, 528		(exp.)
$NOUF_6$ (s)	2421	485, 505	136, 148, 175	(theory)
	2333	509, 551		[10]

NMR-Spectroscopy

Due to the paramagnetic properties of uranium(V) the NMR signals of such species are broadened and the chemical shift is unpredictable in NMR spectroscopy.[46] Probably due to this fact there have been no liquid state and only one solid state NMR spectroscopic investigation of the $NOUF_6$ system.[28] However, from the number of signals the amount of species present in solution can be deduced. Additionally, the paramagnetic shift of the solvent gives information on the interaction of $NOUF_6$ with the solvent. Therefore ^1H and ^{19}F NMR spectra were recorded of a solution of $NOUF_6$ in anhydrous hydrogen fluoride and of a $NOUF_6$ suspension in acetonitrile. To exclude influence from the lock and shim parameters and from the ^1H decoupling frequency in the ^{19}F NMR experiments, spectra of neat hydrogen fluoride and the $NOUF_6$ solutions in HF were recorded in immediate succession to ensure all parameters stayed identical.

The proton signal of HF in the ^1H NMR spectrum of a solution of $NOUF_6$ in anhydrous hydrogen fluoride was observed at 8.84 ppm with a linewidth of 22.5 Hz. This is a downfield shift of 0.46 ppm compared to neat anhydrous hydrogen fluoride, which we observed at 8.38 ppm with a linewidth of 2.4 Hz. The $^1J_{HF}$ coupling constant is 4.5 Hz in both spectra. This trend is more pronounced in the ^{19}F NMR spectrum, where the fluorine signal of HF was observed at −170.38 ppm with a linewidth of 117 Hz (Figure 6), which is a downfield shift of 28 ppm compared to neat hydrogen fluoride (−198.32 ppm, linewidth 13 Hz). This distinct paramagnetic down field shift and line broadening is indicative for a considerable interaction of the paramagnetic UF_6^- moiety with the solvent and is expected if the uranium(V) complex is in solution. The observed chemical shifts of neat anhydrous hydrogen fluoride in the ^1H and ^{19}F NMR spectra are in good agreement with literature values.[47]

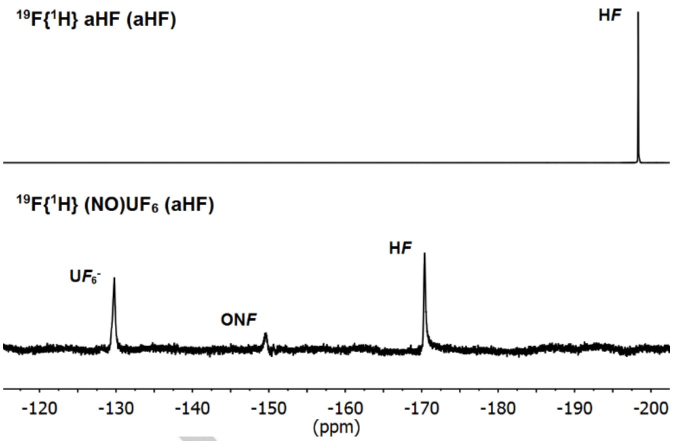

Figure 6. ^{19}F NMR spectrum of anhydrous HF (top) and $NOUF_6$ in anhydrous HF (bottom) at T = 300 K.

Two further signals, at −149.56 and −129.77 ppm with linewidths of 169 and 157 Hz, could be observed in the ^{19}F NMR spectrum. The chemical shift of the prior signal is in good agreement with hydrogen fluoride adducts to nitrosyl fluoride.[48] For example ON*F*·3HF exhibits a signal in the ^{19}F NMR spectrum at −155 ppm, while neat ONF is observed at 478 ppm.[48,49] Nitrosyl fluoride is presumably formed through the fluorination of the NO^+ cation by HF in solution, while the formed proton is distributed through the anhydrous hydrogen fluoride. Various HF adducts to nitrosyl fluoride are known.[50] However, due to the large excess of HF compared to ONF and the dynamic coordination and dissociation of HF to ONF, the stoichiometry of the adduct cannot be deduced. Due to the fast exchange of coordinated and free HF no signal for the coordinated HF can be observed on the NMR time scale. The formation of the nitrosyl fluoride and the adduct formation with HF is presumably one of the main driving forces for the good solubility of $NOUF_6$ in anhydrous hydrogen fluoride compared to other non-aqueous solvents.[10] So, the signal at −129.77 ppm is assigned to the UF_6^--anion, which is consistent with the higher signal intensity compared to the signal of ON*F*·nHF, due to the higher number of fluorine nuclei of the anion. Additionally, an investigation of KUF_6, which will be published elsewhere, shows a signal at a similar chemical shift in in the ^{19}F NMR spectrum in aHF. No further species were observed for $NOUF_6$ in the ^1H and ^{19}F NMR spectra in a range of −45 to 55 ppm and −1150 to 1150 ppm, respectively. The chemical shifts and linewidths of the observed signals are summarized in Table 4.

Table 4. Signals observed in ^{1}H and $^{19}F\{^{1}H\}$ NMR spectroscopy.

	Species	^{1}H / ppm	Linewidth / Hz	^{19}F / ppm	Linewidth / Hz
aHF	HF	8.38	2.4	−198.32	13
	HF	8.84	22.5	−170.38	117
$(NO)UF_6$ in aHF	$ONF \cdot nHF$	-	-	−149.56	169
	UF_6^-	-	-	−129.77	157

In the ^{1}H NMR spectrum of a $NOUF_6$ suspension in acetonitrile no paramagnetic shift for the methyl-proton signal of the solvent could be observed. We therefore assume, that the solubility is too low to yield significant interactions with this solvent. This is also supported by the lack of signals in the ^{19}F NMR spectrum.

EPR-Spectroscopy

For actinoid compounds with a $5f^1$ electron configuration one can observe a strong deviation in their resonance compared with the g value of 2.0023 for the free electron.[25] This behavior can be explained by spin-orbit coupling. Another important factor is the ligand field of the actinoid atom.[23] For polycrystalline $NOUF_6$ we observed an isotropic g tensor value of −0.739 (T = 4 K, linewidth 114 mT), see Figure 7. Any anisotropy of the g tensor remains unresolved at X-band, also allowing an orthorhombic g tensor, which results only in an insignificant small decrease of the least squares parameter of the fit. The signal broadens at room temperature to a linewidth of 393 mT. Our observed values agree with previously reported ones for $NOUF_6$, with $g_0 = -0.740(7)$ (T = 4 K) and −0.748 (T not reported).[27,51] For $NOUF_6$, as well as for other MUF_6 salts (M = Na, Li, Cs), the strength of distortion from O_h symmetry has been calculated and it has been proposed that the UF_6^- ion may have a tendency towards trigonal distortion, which we can confirm based on our findings from single crystal diffraction.[37,51,52] Other hexafluoridouranate(V) compounds exhibit similar g values in the range of −0.71 to −0.78, some examples are listed in Table 5. For UF_6^- moieties the observed g tensors are significantly smaller than the one for the six-fold coordinated uranium atom in α-UF_5 (D_{4h} symmetry), which shows an asymmetric $|g|$ factor of 0.892 (T = 77 K).[53] The g value for UF_6^- seems to be characteristic for this species. Based on EPR spectroscopic data, it has been proposed for UF_5 to form $[UF_4(L)_x]^+$ UF_6^- species (L = solvent molecule) in organic solvents, like acetonitrile or dimethyl sulfoxide.[54] Some theoretical papers cover the calculation of g tensors for UF_6^- compounds.[22,23]

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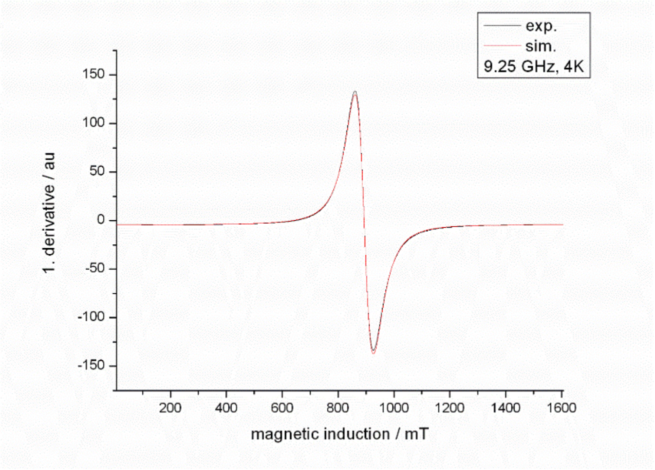

Figure 7. First-derivative EPR spectrum of polycrystalline $NOUF_6$. The black line shows the measured spectrum, the red one the simulated.

Table 5. g_o values of polycrystalline six-fold coordinated uranium(V) compounds.

Species	Crystal system	$\lvert g_o \rvert$	*T* / K	Reference
$NOUF_6$	cubic	0.739	4	present work
		0.740(7)	4	[27]
		0.748	?	[51]
α-UF_5	tetragonal	0.892	77	[53]
$(H_3O)UF_6$	cubic	0.78(10)	77	[55]
$(PPN)UF_6$	triclinic	0.71	100	[33]
$LiUF_6$	rhombohedral	0.768	77	[56]
α-$NaUF_6$	rhombohedral	0.745	?	[51]
β-$NaUF_6$	cubic	0.748	77	[56]
$CsUF_6$	rhombohedral	0.709	77	[56]

Photoluminescence and absorption spectroscopy

The absorption spectrum (blue curve) of $NOUF_6$ is depicted in Figure 8. It shows three closely spaced absorption peaks with the highest one centered between the other two at 1358 nm. The obtained absorption curve is similar to the absorption curves of other hexafluoridouranates(V), e.g. $LiUF_6$, $NaUF_6$ and $CsUF_6$, and to the previously reported one for $NOUF_6$.[20,27] The three equally spaced peaks seem to be typical for the UF_6^- ion. The central one was often interpreted as the pure electronic $\Gamma_7 \rightarrow \Gamma_7'$ transition, with vibronic transitions equally spaced at higher and lower energies.[57]

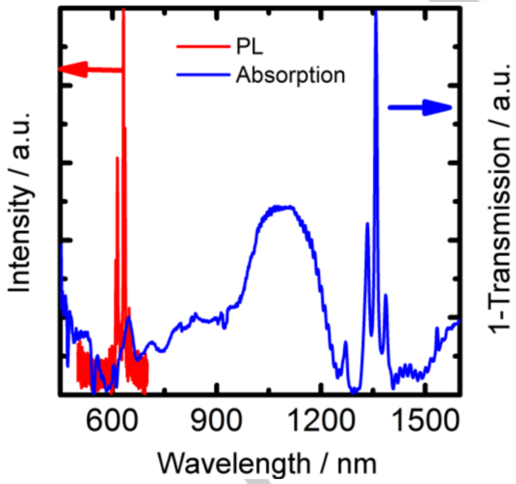

Figure 8. Absorption spectrum (blue curve) and photoluminescence (red curve) of $NOUF_6$.

The photoluminescence (red curve) measured for the same $NOUF_6$ sample displays pronounced peaks at 649.21, 635.89, 632.65, 616.91 and 610.83 nm. However, the photoluminescence is not homogeneous over the whole sample, but could only be measured on some locations. This could be due to an optically non-cubic symmetry of $NOUF_6$, thus leading to a pseudo-cubic symmetry in terms of the single crystal structure, similar to the optical biaxiality and pseudo-hexagonal symmetry of KUF_6, NH_4UF_6 and $RbUF_6$.[17]

Magnetic measurements

Nitrosyl hexafluoridouranate(V) behaves like a Curie paramagnet. The field dependent measurement shows a linear progress with the molar susceptibility of 1.226(2) · 10^{-7} m^3 mol^{-1}at 5 K.

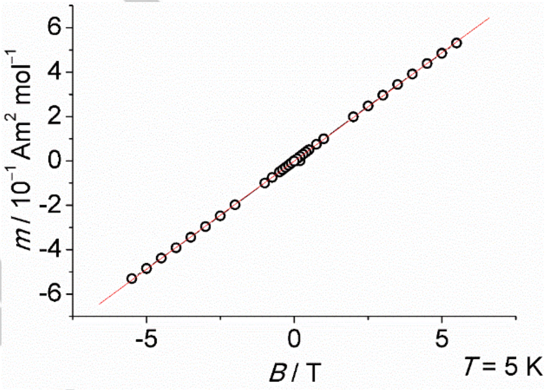

Figure 9. Field dependent data of $NOUF_6$, measured at 5 K.

Due to the strong diamagnetic contribution of $NOUF_6$ of $-1.33 \cdot 10^{-9}$ m^3 mol^{-1}, and the contribution of the sample holder, the value of measured magnetic moment passes zero at around 125 K during the temperature dependent scans. Therefore, in a range from 100 K to 150 K no reliable data is available, and the calculations of the effective paramagnetic moment μ_{eff} of the U(V) ion, as well as a further temperature independent paramagnetic contribution TIP, were done below this critical range. In Figure 10 the molar susceptibility of $NOUF_6$ at different applied fields is shown.

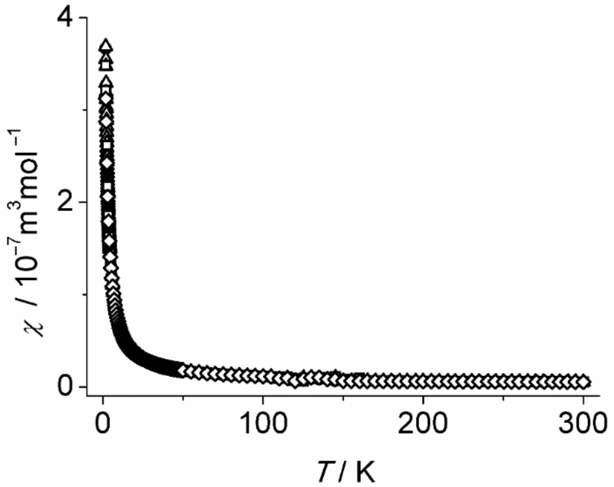

Figure 10. Molar susceptibility of NOUF$_6$, measured with applied fields of 0.1, 0.5, 2 and 5 T.

In order to receive information about $\mu_{\mathrm{eff.}}$, χ_{TIP} and the Weiss constant Θ, a parameter that allows an indication of possible magnetic interactions, a modified Curie-Weiss law was used, see Equation 5.

$$\chi = \chi_{\mathrm{TIP}} + \chi_{\mathrm{CW}} \qquad (5)$$

With χ_{CW} being expressed by the Curie-Weiss law (Equation 6).

$$\chi_{\mathrm{CW}} = \frac{C}{T - \Theta} \qquad (6)$$

In this expression C represents the Curie constant (Equation 7),

$$C = \frac{\mu_{\mathrm{eff}}^2\ N_{\mathrm{A}}\ \mu_{\mathrm{B}}^2}{3\ k_{\mathrm{B}}} \qquad (7)$$

where μ_{eff} is the number of effective magnetic moments in units of Bohr magnetons, N_{A} is Avogadros number, μ_{B} represents the Bohr magneton, and k_{B} the Boltzmann constant. By converting Equation 5 and plotting χ^{-1} or χT vs. T, one can calculate the mentioned parameter. Figure 11 shows different plots of data of the temperature dependent scan at 0.1 T. The resulting values are $4.4(2) \cdot 10^{-9}$ m^3 mol^{-1} for χ_{TIP}, 0.633(1) μ_{B} per formula unit for μ_{eff} and ± 0.04(2) K for Θ. The very small value for Θ and the changing sign indicates no magnetic interaction between the uranium atoms, which is in accordance with the U−U distance of 5.1732(2) Å. The reported data for CsUF$_6$, which has a μ_{eff} of 0.62 μ_{B} below 10 K, are in agreement with ours for the UF$_6^-$ system.[58] No magnetic interaction has been observed to a temperature of 1.5 K. α-UF$_5$, which follows the Curie-Weiss law between 200 and 300 K, shows a μ_{eff} of 2.37 μ_{B} and −148 K for Θ, which indicates strong interactions between the U(V) ions, in accordance with an antiferromagnetic ordering at 6.3 K. The shortest separation of U(V) atoms in α-UF$_5$ is 4.4717(2) Å.[35,59]

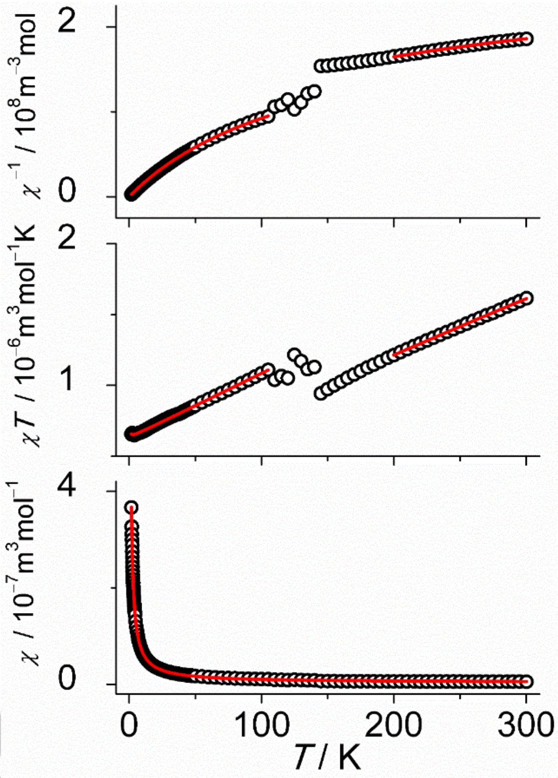

Figure 11. Different plots of the temperature dependent scan at 0.1 T.

Conclusions

Single crystals of nitrosyl hexafluoridouranate(V) can be obtained by reaction of NO with UF$_6$ in aHF. The compound crystallizes in space group $Ia\bar{3}$ (No. 206), with a octahedron-like UF$_6^-$ anion. The deviation of the UF$_6^-$ units from O_{h} symmetry can be deduced from the Raman and IR spectra, which is in accordance with the $.\bar{3}.$ site symmetry of the U(V) atom position in the crystal. The driving force for dissolution in aHF is attributed to the formation of solvated NO$^+$ cations in form of an ONF·nHF adduct, as deduced from ^{19}F NMR spectroscopy. The EPR spectroscopic values and magnetic measurements are typical for a 5f^1 compound, exhibiting differences to the g factor of the free electron and the spin-only value for a single electron, which can be attributed to spin-orbit coupling.

Further studies on the chemical properties of NOUF$_6$, as well as on the crystallographic, magnetic and chemical properties of other hexafluoridouranates(V) are in progress.

Experimental Section

General

All operations were performed in either stainless steel (316L) or monel metal Schlenk lines, which were passivated with 100% fluorine at various pressures before use. Preparations were carried out in an atmosphere of dry and purified Argon (5.0, Praxair). Hydrogen fluoride (99%, Hoechst) was dried over K_2NiF_6. Nitric oxide (≥99.8%, Messer Griesheim) was used; traces of NO_2 were removed in a dry ice/isopropanol cooling bath. Uranium hexafluoride was prepared by reacting UF_4 and F_2 and was used after sublimation.

Preparation of $NOUF_6$

4.77 g (13.6 mmol) UF_6 was placed in a FEP reaction tube by sublimation. Approximately 6 mL of aHF were condensed onto the solid. The gas phase was slowly mixed with NO at room temperature, which was previously passed through a cooling trap at −78 °C, in order to separate traces of H_2O and NO_2. Immediately, a white vapor appeared over the liquid phase and the HF solution turned slightly yellow. After cooling with a dry ice/isopropanol mixture the HF turned blueish. Further NO was added until most of the UF_6 crystals disappeared. The HF was slowly pumped off and a blue-greenish crystalline precipitate formed. Several pumping steps were performed to remove traces of UF_6 and HF. 4.75 g (12.4 mmol, 91.2%) $NOUF_6$ was isolated in the form of blue-green single crystals.

Elemental analysis

The uranium content was determined by atomic emission spectroscopy with a 4200 MP-AES spectrometer (Agilent Technologies). Samples were weighed under an Ar atmosphere and dissolved in concentrated nitric acid prior to analysis. U: calc.: 62.3, found: 62.6%.

Density determination

The density of $NOUF_6$ was measured using the automated gas displacement pycnometry system AccuPyc II 1340 (micromeritics) with a calibrated 0.1 cm^3 sample holder and helium as the gas being displaced. The number of preliminary purges was set to 30, while the subsequent density measurements were done 100 times with further averaging.

Single crystal X-ray diffraction

X-ray structure analysis of single crystals of $NOUF_6$ was carried out with a D8 Quest diffractometer (Bruker) with monochromated molybdenum radiation (Mo-K_α, λ = 0.71073 Å) and a PHOTON 100 CMOS detector. Evaluation and integration of the diffraction data was carried out by using the Bruker APEX2 software, and an empirical absorption correction was applied (multi-scan).[60] The structure was solved using direct methods (SHELXT) in space group $Ia\bar{3}$ (206), and refined against F^2 (SHELXLE).[61,62] All atoms were located by Difference Fourier synthesis and refined anisotropically. Representations of the crystal structure were created using the Diamond software.[63] Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49 7247 808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the depository number CSD-431038.

Powder X-ray diffraction

Powder X-ray diffraction patterns were obtained with a Stadi-MP-Diffractometer (Stoe) using Cu-K_α radiation (λ = 1.54051 Å), a germanium monochromator, and a Mythen1K detector. The data were handled using the WINXPOW software.[64] The compound was filled into Lindemann capillaries and flame-sealed. Le Bail profile fitting and Rietveld refinement was done in the Jana2006 software.[65] To model the peak profile shape, the pseudo-Voigt function was chosen. The background contribution was determined by using Chebyshev polynomials with seven terms. The scale factor, zero angular shift, profile shape parameters and lattice parameters were refined.

IR and Raman spectroscopy

The IR spectrum was measured on an alpha FTIR spectrometer (Bruker) using a diamond ATR unit under an Ar atmosphere. The spectrum was processed with the OPUS software package.[66] The Raman spectrum was collected using a Labram HR 800 (JobinYvon) instrument equipped with a 25 mW He/Ne laser tube (λ = 632.817 nm). The sample of $NOUF_6$ was prepared in a flame-sealed glass capillary under Ar, and the collected data were handled in the LabSpec software.[67]

NMR spectroscopy

^1H and ^{19}F NMR spectra were recorded on an Avance III 500 NMR spectrometer (Bruker) equipped with a Cryo-Probe (Prodigy). ^1H NMR spectroscopy (500.20 MHz) used $SiMe_4$, and ^{19}F NMR spectroscopy (470.66 MHz) used neat $CFCl_3$ as an external reference. Samples were prepared by condensing anhydrous HF onto $NOUF_6$ at −196 °C in 3 mm FEP tubes, which were then sealed under vacuum with a heat gun and subsequently placed in standard 5 mm glass NMR tubes. Chemical shifts are given for 300 K at 1.31 bar hydrogen fluoride vapor pressure. NMR spectra were processed with the MestReNova software.[68]

$NOUF_6$: $^{19}F\{^1H\}$ (aHF): $\delta = -149.56$ ($ONF\cdot nHF$), -129.77 (UF_6^-) ppm.

EPR spectroscopy

EPR measurements of polycrystalline $NOUF_6$ were performed with a modified Varian E15 X-band spectrometer, equipped with a BH-15 field regulator (Bruker) and a helium cryostat (Oxford), controlled by a C program of our own design. Measurements were taken from room temperature down to 4 K. The magnetic field axis was calibrated by using a sample of powdered dpph (g = 2.0036(1)).[69] The modulation amplitude was set to 1 mT at 100 kHz, the microwave power was always below saturation.

Photoluminescence and absorption spectroscopy

The absorption measurements were performed with a tungsten lamp. The white light was transmitted through the sample and detected with an Optical Spectrum Analyzer (ANDO AQ-6315A). The photoluminescence measurements were performed with a 445 nm continuous wave Laser with a power of 27 mW focused on an approximately 100 µm small area on the sample and detected with the same Optical Spectrum Analyzer. The excitation power of 27 mW lies below the damage threshold of the sample. The samples were prepared in a glass tube filled with inert gas for the photoluminescence measurements. For the absorption measurements, the samples were measured as suspensions in perfluorinated polyether oil (Fomblin Y/VAC 06/6, Solvay) between two quartz plates. The obtained spectrum, which is plotted as 1-transmission, is not related to any features from the oil. The absorption curve is an average over six measurements on different locations on the sample. This was done to minimize the effects of different particle densities on the sample. The absorption curve was corrected by a background.

Magnetic measurements

Magnetic measurements on $NOUF_6$ were carried out with a mpms squid magnetometer (Quantum Design). Field and temperature dependent magnetic data were recorded. The former in the range of −5.5 T to 5.5 T at a constant temperature of 5 K. Temperature dependent scans from 1.8 K to 300 K were measured with applied fields of 0.1; 0.5; 2 and 5 T. The collected data were corrected with respect to the diamagnetic contribution of the KEL-F sample holder, as well as to the diamagnetic moment of the sample derived from Pascal constants taking the composition of $NOUF_6$ into account.

Computational details

The structure, energetics, and the vibrational spectra of $NOUF_6$ were investigated with the CRYSTAL14 program package, using the PBE0 hybrid density functional method.[70–73] For uranium, a triple-zeta-valence level basis set was applied (TZVP), while for the lighter atoms split-valence + polarization (SVP) level basis sets were applied (see Supporting Information for additional basis set details). The reciprocal space was sampled using a 4x4x4 Monkhorst-Pack-type *k*-point grid. Because the $NOUF_6$ is magnetic, spin-unrestricted calculations were carried out. For the evaluation of the Coulomb and exchange integrals (TOLINTEG), tight tolerance factors of 8, 8, 8, 8, and 16 were used. Both the atomic positions and lattice constants were fully optimized within the constraints imposed by the space group symmetry. Default optimization convergence thresholds and an extra large integration grid (XLGRID) for the density-functional part were applied in all calculations. The harmonic vibrational frequencies were obtained by using the computational scheme implemented in CRYSTAL.[74,75] The Raman intensities were obtained using the scheme implemented in CRYSTAL14.[76,77]

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Keywords: uranium • fluorine • X-ray diffraction • anhydrous hydrogen fluoride • hexafluoridouranate(V)

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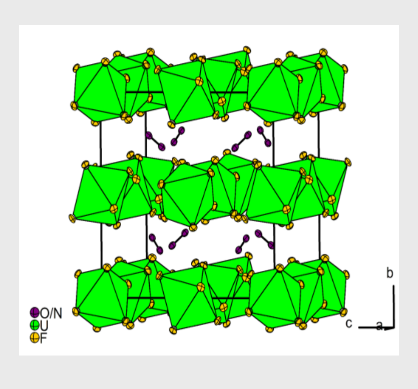
Entry for the Table of Contents

FULL PAPER

Synthesis of NOUF$_6$ by direct reaction of NO with UF$_6$ in anhydrous HF. Investigation of the crystal structure of the hexafluoridouranate(V) by single-crystal X-ray diffraction, as well as theoretical calculations. Magnetic measurements of the compound and reinvestigation of spectroscopic properties.



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NOUF$_6$ revisited. A comprehensive study of a hexafluoridouranate(V) salt.