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A 1D Coordination Polymer of UF₅ with HCN as a Ligand – $\text{UF}_5(\text{HCN})_2$**

Benjamin Scheibe, Stefan S. Rudel, Magnus R. Buchner, Antti J. Karttunen, and Florian Kraus*

Dedicated to Professor Karl O. Christe on the occasion of his 80th birthday

Abstract: We have reacted β-uranium(V) fluoride with liquid anhydrous hydrogen cyanide and obtained a 1D coordination polymer with the composition $[\text{UF}_5(\text{HCN})_2]_\infty$, revealed by single crystal X-ray structure determination. The reaction system was furthermore studied by means of vibrational and NMR spectroscopy, as well as quantum chemical calculations. The compound presents the first described polymeric Lewis adduct and the first HCN adduct of a uranium fluoride.

While f-element coordination chemistry with the cyanide ion (CN⁻) as a ligand is quite well established, there is a noteworthy lack of compounds with its conjugated acid, namely hydrogen cyanide (HCN), as a ligand.[1] This may be attributed to the more difficult handling of HCN in comparison to cyanide salts and its quite high toxicity for human beings,[2,3] Nonetheless, Wöhler probably described the first Lewis adduct of a hydrogen cyanide (HCN) upon warming, whilst pnictogen fluoride HCN adducts, which were used in liquid phase turns turquoise and immediately leads to a color change of the solid to pale green (see SI for photographs). After only a few minutes of reaction time at 0 °C the liquid phase turns turquoise and already after a few hours turquoise needle-shaped crystals separate. The crystallized compound was identified as $[\text{UF}_5(\text{HCN})_2]$ (1) by means of SCXRD. Scheme 2 shows the reaction equation.

$\text{UF}_5(\text{H}) + 2 \text{HCN} \rightarrow [\text{UF}_5(\text{HCN})_2]_\infty$

Scheme 2. Formation of coordination compound 1 from β-UF₅ in liquid HCN.

Compound 1 crystallizes in the orthorhombic crystal system in space group Pca2₁ (No. 29) with Z = 4 (see exp. section for further crystallographic details). A section of the crystal structure is shown in Figure 1. Each uranium atom is coordinated by five fluorine atoms, of which two are μ-bridging, and two adjacent HCN molecules, forming a coordination polyhedron shaped like a trigonal-dodecahedron. The compound can thus be regarded as a one-dimensional coordination polymer described with the Niggli representation $[\text{UF}_5(\text{HCN})_2]_\infty$.[19] The U-F (2.014(5)–2.071(6) Å) and U-F$_{\text{μ}}$ (2.272(6)–2.330(5) Å) atomic distances of compound 1 in the crystal structure are comparable to those of both known pure uranium(V) fluorides, showing only minor increases of the atomic distances due to the coordination of HCN molecules (μ-UF₅).$[\text{UF}_5(\text{F})_2]_n$, T = n.a., distances [Å]: U-F 2.020(5), U-F$_{\text{μ}}$ 2.236(1); $\text{UF}_5(\text{F})_2$, T = RT, distances [Å]: U-F 1.96(2), U-F$_{\text{μ}}$ 2.27(2).[20,21] The C-F interchain atomic distances (2.963(2)–3.212(2) Å) are in the range of possible, however quite weak hydrogen bonding with resulting a CHF angles in the range of 110.1–156.3°. This may promote the...
adjacent coordination mode of the HCN ligands and strengthen the interchain bonding interaction. The U–N atomic distances (2.643(8)–2.735(8) Å) and αCNU angles (168.1(9)–178.4(8)°) of compound 1 are different due to space group symmetry and this different bonding of HCN ligands is further supported by the Raman and IR spectra. There, two bands for C–N stretching modes are present (see Figure 2 and 3). If one compares the C–N atomic distances (1.113(1)–1.145(1) Å) of compound 1 with other HCN Lewis adducts like VCl$_2$·2HCN (1.13(1) Å, T = n.a.), [TiCl$_4$(HCN)$_3$] (1.11(1) Å, T = n.a.), or H[NbCl$_4$(CN)] (1.090(4) Å, T = n.a.), only a significant difference can be seen for the latter one.$^{[6,22,23]}$ This can be attributed to the quite strong interaction in the niobium compound, leading to a rise in the acidity and thus the formation of the [NbCl$_4$(CN)]$^-$ anion.$^{[15]}$ The comparison with the C–N atomic distance in the gas phase (1.157 Å) also speaks for a rather weak interaction of HCN with UF$_5$.\cite{24}

Figure 1. Section of the crystal structure of compound 1. Infinite chains are truncated (dots) and an exemplary coordination polyhedron around a uranium atom is shown. Displacement ellipsoids are shown at the 70% probability level at 100 K, hydrogen atoms are depicted isotropic with arbitrary radii.

To verify the coordination of the HCN molecules via the N atoms, which in this case could not be unambiguously shown by the X-ray structure determination, Raman and ATR-IR spectra of compound 1 were collected. The Raman spectrum of turquoise crystals of compound 1 shows three distinct bands at 2135, 2131 and 599 cm$^{-1}$ beneath the lattice modes, which can be attributed to C–N and U–F stretching modes (Table 1 and Figure 2).\cite{25,26} The first two bands are shifted hypsochromic in comparison to the mode of liquid HCN and the latter U–F mode is shifted bathochromic with regard to α- and β-UF$_5$. The initial ATR-IR spectrum of time dependent measurements of a powdered sample of compound 1, which were measured in a glovebox under an Ar atmosphere, shows characteristic bands of HCN at 3222, 2137 and 781 cm$^{-1}$, respectively (Table 2 and Figure 3). One could come up with the idea that HNC would form and coordinate via the carbon atom. However, the bands of a HNC molecule in an Ar matrix appear at 3620, 2029 and 477 cm$^{-1}$. Also, there is an enthalpy difference of approx. 62 kJ/mol to the HCN molecule, thus making the formation and coordination of HNC molecules very unlikely.$^{[27,28]}$ We also calculated the Raman and IR spectra using quantum chemical methods (DFT-PBE0), and the calculated peak positions listed in Table 1 are in very good agreement with the experimental data (full spectral figures and assignment are available in the Supporting Information). The computationally calculated spectra also make it possible to distinguish between U–F (non-bridging) and U–F$_5$ (bridging F) stretching vibrations. The latter occur at about 70–100 cm$^{-1}$ lower energy in comparison to the former, thus lying in the far IR range, which was not measured. This is in line with the results from a population analysis, which suggests that the U–F$_5$ (bridging) bonds are slightly more ionic in comparison to the non-bridging U–F bonds.

Table 1. Raman spectroscopic data of α- and β-UF$_5$ in comparison to compound 1. All values are given in [cm$^{-1}$].

<table>
<thead>
<tr>
<th>Species</th>
<th>ν(C–N) (theory)</th>
<th>ν(U–F) (theory)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-UF$_5$</td>
<td>3210</td>
<td>790</td>
<td>530</td>
</tr>
<tr>
<td>β-UF$_5$</td>
<td>3222</td>
<td>2137</td>
<td>781</td>
</tr>
</tbody>
</table>

Figure 2. Room temperature Raman spectrum of turquoise crystals of compound 1 under liquid HCN. The band at 2094 cm$^{-1}$ is assigned to ν(C–N) of liquid HCN by comparison to the literature.
The applicability of NMR spectroscopy for the analysis of uranium(V) is limited due to its paramagnetism. Therefore, the chemical shift is unpredictable and the signals are broadened, sometimes to an extent that they are not observable.[39,40] To the best of our knowledge there is currently only one solution NMR spectroscopic investigation on UF₆ and its derivatives in acidic media (anhydrous HF) and only one solid state NMR spectroscopic characterization of α-UF₆.[32,33] The number of NMR spectroscopic studies with αHCl as solvent is very small and focus mainly on the physicochemical properties.[34,35]

To gain insight into the solution state of β-UF₆ we recorded ¹H and ¹⁹F NMR spectra of solutions in αHCl. The solvent signal (αHCl solutions of UF₆) is observed at 6.63 ppm with a line width of 8.4 Hz in the ¹H NMR spectrum. In comparison, the signal of neat HCN is observed at 5.95 ppm with a line width of 9.0 Hz. This distinctive paramagnetic down field shift of ¹H nuclei with the paramagnetic uranium(V) atoms, which can cause extreme line broadening. Additionally, the fluorine nuclei are probably chemically inequivalent due to a coordination polyhedron which we assume to be related to or derived from the one in the crystal structure. We suppose that five fluorine nuclei and an unknown number of HCN molecules are coordinated. This leads to smaller signals, since several individual signals rather than one mutual signal are present, and to even further broadening, if site exchange occurs. Due to the induced polymerization of HCN at ambient temperature no larger spectroscopic windows could be explored, while the high melting point of −13 °C HCN paired with the relatively low solubility of β-UF₆ excluded variable temperature NMR experiments.

We took insight into the β-UF₆/HCN system and found that a coordination polymer, [UF₆(HCN)₅], is formed, which was an unknown structural feature for HCN Lewis adducts. The interaction of HCN is only weak, thus the compound easily gives off HCN in vacuo and Ar. The calculated IR and Raman spectra show a good agreement with experimental data and allow a full assignment of bands. Further studies regarding αHCl as a solvent for uranium compounds are underway.

Figure 3. Time dependent room temperature ATR-IR spectra of compound 1 measured under Ar atmosphere. For comparison, the ATR-IR spectrum of β-UF₆ is also shown (top).

Experimental Section

**Caution!** The toxicity of hydrogen cyanide or its solutions should not be underestimated.[2,3] Working under a well ventilated fume hood is mandatory, a HCN-detector and butyl rubber gloves are recommended. Furthermore we cannot yet recommend the advice of Gattermann to smoke cigars during the work with HCN. We could not recognize the described ‘special’ taste whilst smoking near an open bottle full of KCN beyond doubt but further studies are underway[36] General: All operations with UF₆ were performed either in stainless steel (316L) or in Monel metal Schlenk lines, which were passivated with 100% fluorne at various pressures before use. Preparations were carried out on a glovebox. Preparations were carried out in an atmosphere of dry and purified argon (5.0, Praxair). UF₆ was prepared by reacting UF₅ and F₂ and was used after sublimation. β-UF₆ was prepared by photoreduction of UF₆ with CO in a fused quartz apparatus, according to a literature procedure.[37] Anhydrous HCN was prepared from KCN and H₂SO₄ and purified by several distillation steps and finally stored over 4 Å-Molecular sieves[38].

Synthesis: 1. β-UF₆ was placed in a Schlenk tube and cooled with liquid nitrogen. An excess of αHCl was added by vacuum distillation. The mixture was warmed to 0 °C with an ice bath. After a short time the solid turned light green to turquoise and after a few hours turquoise crystals of compound 1 were formed, which are suitable for SCXRD. Samples were measured by several days at 0 °C a brown amorphous product also is formed, which is considered to be a polymerization product of HCN.[39] Photographs of the reaction mixture can be found in the SI.

Single crystal X-ray diffraction: X-ray structure analysis of a single crystal of compound 1 was carried out with a D8 Quest diffractometer (Bruker) with monochromated molybdenum radiation (MoKa λ = 0.71073 Å) and a PHOTON 100 CMOS detector. Evaluation and integration of the diffraction data was carried out using the Bruker-APEX2 software, and an empirical absorption correction was applied (multi-scan).[40] The structure was solved by using direct methods (SHELXTL) in the space group type Pca2₁ (29), and refined against F² (SHELXLX) as an inversion twin.[41,42] All atoms were located by difference Fourier synthesis and refined anisotropically, hydrogen atoms were located and refined using a riding model. Representations of the crystal structures were created by using the Diamond software.[43] Crystallographic data: C₃F₅H₅N₃U₂ (M = 367.07 g mol⁻¹), crystal size 0.087(0.039, 0.051, 0.151) mm, orthorhombic, Pca2₁ (No. 29); a = 23.047(1), b = 8.521(1), c = 14.369(1) Å; V = 2821.7(3) Å³, Z = 4, p(MoKa) = 3.645 g cm⁻³, μ(MoKa) = 23.03 mm⁻¹, λ(MoKa) = 0.71073 Å, T = 100 K, Dcalc = 30.60 g cm⁻³. Data, parameter, restraints: 8631, 371, 1; R(w) = 0.050; R(F²) (1 ≤ 2.1σ(F²), all data): 0.034, 0.034, wR(F²) (1 ≤ 2.1σ(F²), all data): 0.087; Δmax/min = 5.58 / 4.03 e Å⁻³, BASF = 0.21(1). Further details of the crystal structure investigation can be obtained from the Cambridge Structural Database (http://www.ccdc.cam.ac.uk) on quoting the deposition number CCDC-1511349.

Computational details: The calculations were carried out with the CRYSTAL14 program package, using the PBEO hybrid functional method.[44,45] Full computational details are given in the Supporting information.

IR and Raman Spectroscopy: The IR spectra were measured on a PerkinElmer FTIR spectrometer (Bruker) by using a diamond ATR unit under an Ar atmosphere in a glovebox. The spectra were processed with the OPUS software package.[46] The Raman spectrum was collected using a Labram HR800 (JobinYvon) instrument equipped with a 25 mW He/Ne laser tube (λ = 632.817 nm). The sample of compound 1 was prepared in a flame-sealed glass capillary under Ar shortly before the measurement. Turquoise crystals were measured, and the data was collected with the LabSpec software.[47]

NMR spectroscopy: ¹H and ¹⁹F NMR spectra were recorded on an Avance III HD 300 NMR spectrometer (Bruker). ¹H NMR spectroscopy (300.25 MHz) used SiMe₄ and ¹⁹F NMR spectroscopy (282.62 MHz) used neat CFCs as an external reference. Samples were prepared by condensing αHCl onto β-UF₆ at −78 °C in J.-Young NMR tubes. Chemical shifts are given for 300 K at 1.04 bar hydrogen cyanide vapor pressure.[48]

Keywords: coordination polymer • fluorides • cyanides • uranium • X-ray diffraction


COMMUNICATION

Entry for the Table of Contents

COMMUNICATION

UF₅/HCN: The system of β-uranium(V) fluoride and HCN was studied. The crystal structure of a polymeric HCN adduct is presented. The compound was studied by means of quantum chemical methods, as well as by vibrational spectroscopy.

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