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A 1D Coordination Polymer of UF$_5$ with HCN as a Ligand – $^{1}$\textsubscript{∞}$[\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 80$^{th}$ birthday

Abstract: We have reacted \(\beta\)-uranium(V) fluoride with liquid anhydrous hydrogen cyanide and obtained a 1D coordination polymer with the composition $[\text{UF}_5(\text{HCN})_2]^{-1}$, revealed by single crystal X-ray structure determination. The reaction system was furthermore studied by means of vibrational and NMR spectroscopy, as well as by 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 with its conjugated acid, namely hydrogen cyanide (HCN), as a ligand.$^{[1]}$ Nonetheless, Wöhrler probably described the first Lewis adduct of a transition metal and HCN, $[\text{TiCl}_4(\text{HCN})_2]$, revealed by chemical analysis, in 1850.$^{[2,3]}$

Only a few more HCN Lewis adducts have been described to date, mainly of transition metal and main group element compounds. Most of them are halides and covered in a review by Corain in 1982.$^{[4]}$ Furthermore, HCN can act as a ligand towards the Xe$^+$ cation, as observed in $[\text{Xe}(\text{NCH})_2]\text{[AsF}_5]$. A selection of compounds known from the literature is shown in Scheme 1. These can be categorized into room temperature stable and unstable towards HCN loss, which indicates the strength of interaction. For example, the beryllium chloride adduct, $\text{BeCl}_2\cdot\text{HCN}$, easily loses HCN upon warming, whilst pnicogen fluoride HCN adducts, $[\text{EP}_5(\text{HCN})]\ (\text{E} = \text{As, Sb})$ are thermally quite stable solids, which degrade at temperatures of 85°C or higher.$^{[5-7]}$

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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 sCN 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\textsubscript{2}−2HCN (1.13(1) Å, T = n.a.), [TiCl\textsubscript{3}(HCN)\textsubscript{2}] (1.11(1) Å, T = n.a.), or H[NbCl\textsubscript{3}(CN)] (1.09(4) Å, T = n.a.), only a significant difference can be seen for the latter one.\textsuperscript{[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\textsubscript{3}CN\textsuperscript{−}] anion.\textsuperscript{[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\textsubscript{5}.\textsuperscript{[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\textsuperscript{−1} beneath the lattice modes, which can be attributed to C−N and U−F stretching modes (Table 1 and Figure 2).\textsuperscript{[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\textsubscript{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\textsuperscript{−1}, respectively (Table 2 and Figure 3). One could come up with the idea that HNC would form and coordination of HNC molecules in an Ar matrix appear at 3620, 2029 and 477 cm\textsuperscript{−1}. Also, there is an enthalpy difference of approx. 82 kJ/mol to the HCN molecule, thus making the formation and coordination of HNC molecules very unlikely.\textsuperscript{[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\textsubscript{β} (bridging F) stretching vibrations. The latter occur at about 70–100 cm\textsuperscript{−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\textsubscript{β} (bridging) bonds are slightly more ionic in comparison to the non-bridging U−F bonds.

<table>
<thead>
<tr>
<th>Species</th>
<th>ν(C−N) (cm\textsuperscript{−1})</th>
<th>ν(U−F) (cm\textsuperscript{−1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-UF\textsubscript{5}</td>
<td>-</td>
<td>628</td>
<td>[25]</td>
</tr>
<tr>
<td>β-UF\textsubscript{5}</td>
<td>-</td>
<td>614</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2135, 2131</td>
<td>599</td>
<td>(exptl)</td>
</tr>
<tr>
<td>2190</td>
<td>589</td>
<td>(theory)</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Raman spectroscopic data of α- and β-UF\textsubscript{5} in comparison to compound 1. All values are given in [cm\textsuperscript{−1}].

<table>
<thead>
<tr>
<th>Species</th>
<th>ν(C−H) (cm\textsuperscript{−1})</th>
<th>ν(C−N) (cm\textsuperscript{−1})</th>
<th>δ(H−C−N) (cm\textsuperscript{−1})</th>
<th>ν(U−F) (cm\textsuperscript{−1})</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>HCN\textsubscript{0}</td>
<td>3215</td>
<td>2096</td>
<td>794</td>
<td>-</td>
<td>[25]</td>
</tr>
<tr>
<td>α-UF\textsubscript{5}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>580</td>
<td>[25]</td>
</tr>
<tr>
<td>β-UF\textsubscript{5}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>573</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3222</td>
<td>2137</td>
<td>781</td>
<td>511</td>
<td>(exptl)</td>
</tr>
<tr>
<td>3210</td>
<td>2190</td>
<td>790</td>
<td>530</td>
<td>(theory)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. IR spectroscopic data of HCN, α- and β-UF\textsubscript{5} in comparison to compound 1 (initial measurement). All values are given in [cm\textsuperscript{−1}].

Figure 2. Room temperature Raman spectrum of turquoise crystals of compound 1 under liquid HCN. The band at 2094 cm\textsuperscript{−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. To the best of our knowledge there is currently only one solution NMR spectroscopic characterization of α-UF₅. The number of NMR spectroscopic studies with aHCN as solvent is very small and focus mainly on the physicochemical properties.

To gain insight into the solution state of β-UF₅ we recorded ¹H and ¹⁹F NMR spectra of solutions in aHCN. The solvent signal (aHCN solutions of UF₅) 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 downfield shift of the signal of neat HCN is observed at 5.95 ppm is evidence for coordination on UF₅, 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-UF₅ excluded variable temperature NMR experiments.

We took insight into the β-UF₅/HCN system and found that a coordination polymer, [UF₅(HCN)]ₙ, 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 on 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 aHCN as a solvent for uranium compounds are underway.

Experimental Section

Caution! The toxicity of hydrogen cyanide and its solutions should not be underestimated. 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.

General: All operations with UF₅ were performed either in stainless steel (316L) or in 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). UF₅ was prepared by reacting UF₃ and F₂ and was used after sublimation. β-UF₅ was prepared by photoejection of UF₅ with CO in a fused quartz apparatus, according to a literature procedure. Anhydrous HCN was prepared from KCN and H₂SO₄ and purified by several distillation steps and finally stored over 4Å (Mirco) and SiP₅ (Merck). Synthesis. A β-UF₅ was placed in a Schlenk tube and cooled with liquid nitrogen. An excess of aHCN 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 were suitable for SCXRD. Additionally, samples were prepared by several days at 0 °C a brown amorphous product also is formed, which is considered to be a polymerization product of HCN. 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 (MoKα = 0.71073 Å) and a PHOTON 100 CMOS detector. Evaluation and integration of the diffraction data was carried out using the Bruker X-RED software and an empirical absorption correction was applied (multi-scan).[40] The structure was solved by using direct methods (SHELXLK) in the space group type Pca2₁ (29), and refined against F² (SHELXL) as an inversion twin. 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.[41] Crystallographic data: C₂H₄N₅U₂ (M = 387.07 g mol⁻¹), crystal size 0.39·0.51·0.034 mm, orthorhombic, Pca2₁ (No. 29); a = 23.047(1) Å, b = 8.521(1) Å, c = 14.369(1) Å; V = 2821.7(3) Å³, Z = 4, ρcalc = 3.645 g cm⁻³, μ(MoKα) = 23.03 mm⁻¹, μ(MoKβ) = 0.71073 Å, T = 100 K, βmax = 30.6°. Data, parameter, restraints: 8631, 371, 1; R = 0.050; R(F) (I≥2σ(I), all data): 0.034, 0.034; wR(F) (I≥2σ(I), all data): 0.087; Δρmax(Δρmin) = 5.58/−1.88 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 CRYSTAL14 program package, using the PBE0 hybrid function method.[42,43] Full computational details are given in the Supporting information.

IR and Raman Spectroscopy: The IR spectra were measured on a Bruker 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.[44] The Raman spectrum was collected by using a Jobin Yvon (Bruker) 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 collected were handled with the LabSpec software.[45] NMR spectroscopy: ¹H and ¹⁹F NMR spectra were recorded on a Varian 300 NMR spectrometer (Bruker). ¹H NMR spectroscopy (300.25 MHz) used SiMe₄ and ¹⁹F NMR spectroscopy (282.62 MHz) used neat COCl₂ as an external reference. Samples were prepared by condensing aHCN onto β-UF₅ at -78 °C in J.-Young NMR tubes. Chemical shifts are given for 300 K at 1.04 bar hydrogen cyanide vapor pressure.[46]

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

COMMUNICATION

The system of $\beta$-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.

B. Scheibe, S. S. Rudel, M. R. Buchner, A. J. Karttunen, F. Kraus

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