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A 1D Coordination Polymer of UF₅ with HCN as a Ligand – $^{1}_{\infty}[UF_{5}(HCN)]_{2}$**

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

**COMMUNICATION**

**Abstract:** We have reacted β-uranium(V) fluoride with liquid anhydrous hydrogen cyanide and obtained a 1D coordination polymer with the composition $[UF_{5}(HCN)]_{2}$, 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 to cyanide salts and its quite high toxicity for human beings.[2,3] Nonetheless, Wöhler probably described the first Lewis adduct of a transition metal halide with HCN, [(TiCl₄(HCN))₂], revealed by chemical analysis, in 1850.[4,5]

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.[6] Furthermore, HCN can act as a ligand towards the XeF₂ cation, as observed in [Xe(NCH)₂F][AsF₆].[7] A selection of compounds known from the literature is shown in Scheme 1. These can be categorized into room temperature stable and unstable towards the loss of HCN, which indicates the strength of interaction. For example, the beryllium chloride adduct, BeCl₂·HCN, easily loses HCN upon warming, while the pricotin fluoride HCN adduct, [EF₅(HCN)] (E = As, Sb) are thermally quite stable solids, which degrade at temperatures of 85 °C or higher.[8,9]

Regarding the reactivity of HCN to uranium halides, little is known: The reported attempts of chemical conversion, these are UCl₄ by Bagnall and coworkers and UF₅ by Klapdike and coworkers, did only result in the formation of an adduct in the first case, which was however not further characterized.[16,17] In the latter case it was assumed, that the formation of a heptacoordinated uranium(VI) species does not occur due to kinetic reasons.

The reported solubility of β-UF₅ in acetonitrile and benzonitrile, as well as in other organic solvents, drew our interest to the β-UF₅/HCN system.[18] The action of liquid anhydrous HCN (aHCN) onto pale green β-UF₅ immediately leads to a color change of the solid to olive 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 $[UF_{5}(HCN)]_{2}$ (1) by means of SCXRD. Scheme 2 shows the reaction equation.

**Scheme 1.** Selection of known transition metal and main group halide Lewis adducts with HCN as a ligand: a) beryllium chloride HCN adduct,[8] b) boron halide HCN adducts,[10-13] c) hexametallorhodanolate(II) bis-(increased) HCN adducts,[14] d) titanium(IV) halide cyanide acids,[15] e) niobium(H) halide cyanide acids,[16] f) pricotin fluoride HCN adducts.[17]

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

Compound 1 crystallizes in the orthorhombic crystal system in space group type $Pnma$: $a = 29.49(8)$ Å, $b = 8.20(2)$ Å, $c = 8.73(2)$ Å, $a = 90°$, $b = 90°$, $c = 90°$. 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 $[UF_{5}(HF)]_{2}[HF]_{3}$.[19]

The U–F (2.014(5)–2.071(6) Å) and U–F$_{\text{CN}}$ (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 (β-UF₅,$^{[1]_{[UF_{5}(HF)]_{2}}}$). $T = n.a.,$ distances [Å]: U–F 2.02(0)(5), U–F$_{\text{CN}}$ 2.236(1); β-UF₅,$^{[2]_{[UF_{5}(HF)]_{2}}}$ $T = RT,$ distances [Å]: U–F 1.96(2), U–F$_{\text{CN}}$ 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 α 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 sCNU 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 VCl₂–2HCN (1.13(1) Å, T = n.a.), [TiCl₄(HCN)₂] (1.11(1) Å, T = n.a.), or H[NbCl₅CN] (1.09(4) Å, T = n.a.), only a significant difference can be seen for the latter one. 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 [NbCl₅CN]⁻ anion. 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 UF₅.

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). 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-UF₅. 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. 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–F₅ (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–F₅ (bridging) bonds are slightly more ionic in comparison to the non-bridging U–F bonds.

| Table 1. Raman spectroscopic data of α- and β-UF₅ in comparison to compound 1. All values are given in [cm⁻¹]. |
|-----------------|-------------|---------------|-------------|-----------------|
| Species        | ν(C–N)      | ν(U–F)        | Ref.        |
| α-UF₅          | -           | 628           | [29]        |
| β-UF₅          | -           | 614           |             |
| 1              | 2135, 2131  | 599           | (exptl)     |
|                | 2190        | 589           | (theory)    |

| Table 2. IR spectroscopic data of HCN, α- and β-UF₅ in comparison to compound 1 (initial measurement). All values are given in [cm⁻¹]. |
|-----------------|-------------|---------------|-------------|-----------------|
| Species        | ν(C–H)      | ν(C–N)        | δ(H–C–N)    | ν(U–F)          | Ref.        |
| HCN₀           | 3215        | 2096          | 794         | -               | [29]        |
| α-UF₅          | -           | -             | -           | 580             | [29]        |
| β-UF₅          | -           | -             | -           | 573             |             |
| 1              | 3222        | 2137          | 781         | 511             | (exptl)     |
|                | 3210        | 2190          | 790         | 530             | (theory)    |

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.
Experimental Section

Caution! The toxicity of hydrogen cyanide or 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 with F₂ and was used after sublimation. β-UF₅ was prepared by photoelectron 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 silica (Merck).

Synthesis: 1: UF₅ was placed in a Schlenk tube and cooled with liquid nitrogen. An excess of aHCHN 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 condensation product I were formed, which are suitable for SCXRD. The compound is paramagnetic and purple crystals of the compound also is formed, which is considered to be a polymerization product of HCN. Photographs of the reaction mixture can be found in the SI.

Crystal single 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, λ = 0.7103 Å) and a PHOTON 100 CMOS detector. Evaluation and integration of the diffraction data was carried out using the Bruker-PIXE software, and an empirical absorption correction was applied (multi-scan). The structure was solved by using direct methods (SHELXTL) in the space group type Pca2₁ (29), and refined against $F^2$ (SHELXLE) 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 structure were created using the Diamond software. Crystallographic data: C₂₃H₄₄N₄U₄ (M = 397.07 g mol⁻¹), crystal size 0.09·0.05·0.01 mm³, orthorhombic, Pca2₁ (No. 29); a = 23.047(1), b = 8.521(1), c = 14.369(1) Å; V = 2821.73(7) Å³, Z = 4, $\rho_{calc} = 3.645$ g cm⁻³, $\mu$(MoKα) = 23.03 mm⁻¹, $\lambda$(MoKα) = 0.71073 Å, $T = 100$ K. $\theta_{max} = 30.60$°; Data, parameter, restraints: 8631, 371, 1; R(adj) = 0.050; R(F) (I ≥ 2σ(F), all data): 0.034, 0.034; wR(F) (I ≥ 2σ(F), all data): 0.087; $\Delta/\sigma$(max) = 5.58 / 1.88 e Å⁻³, BASF = 0.21(1). Further details of the crystal structure investigation can be obtained from the Cambridge Crystallographic 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 PBE0 hybrid density functional method. Full computational details are given in the Supporting information.

IR and Raman Spectroscopy: The IR spectra were measured on an alpha FTIR spectrometer (Bruker) using a diamond ATR unit under an Ar atmosphere in a glovebox. The spectra were processed with the OPUS software package. The Raman spectrum was collected by 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 collected were handled with the LabSpec software.

NMR spectroscopy: ¹H and ¹⁹F NMR spectra were recorded on an Avance II 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 evaporating aAHCN 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.

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

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.