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[UCl₄(HCN)₄] – a hydrogen cyanide complex of uranium tetrachloride[†]

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The reaction of uranium tetrachloride with anhydrous liquid hydrogen cyanide yields a turquoise microcrystalline powder of tetrachlorido-tetraformonitrileuranium(IV), [UCl₄(HCN)₄]. We determined the crystal structure of this compound by powder neutron diffraction. The compound was further characterized by IR spectroscopy and thermogravimetric analysis as well as by magnetic measurements. The paramagnetic compound crystallizes in the tetragonal space group type $I\overline{4}$. To the best of our knowledge this compound represents the first structurally elucidated uranium(IV) complex with HCN as a ligand.

Compared to the multitude of known cyanide complexes of the transition metals, only a few examples have been reported for uranium, and no pseudobinary uranium cyanides have been synthesized to date.¹⁻⁸ In contrast, however, coordination compounds of the free prussic acid are extremely rare in comparison, irrespective of the central atom.9-23 We tend to ascribe this to the difficulties that arise during handling the highly toxic hydrogen cyanide, a liquid, with a boiling point just above room temperature that additionally tends to polymerize. Depending on the conditions, the latter can even lead to explosions.^{24,25} While cyanide salts of monovalent cations, for example of the alkali metals, are slightly soluble in liquid anhydrous HCN (aHCN), ionic compounds of higher valent metals are practically insoluble in it.^{24,25} However, with Lewis acidic compounds of more covalent character, like BeCl₂, BCl₃, VCl₄, or NbCl₅, hydrogen cyanide acts as a Lewis base and forms adducts. These are supposedly dissolved in the form of the respective molecular formonitrile complexes.13,16,22,23 The sublimeable TiCl₄·2HCN, which was the first described HCN



Fig. 1 The structure of the $[UCl_4(HCN)_4]$ molecule in its solid state compound. Isotropic displacement parameters at 70% probability at 50 K for all atoms.

adduct,⁹ was reported to be partially reduced to Ti(m) by warming to 60 °C in liquid aHCN,¹⁹ and to form TiN upon pyrolysis of the gaseous compound.²⁶ Stable HCN adducts thus might be promising starting compounds for hard or refractory nitride coatings.

Bagnall and coworkers observed a reaction of UCl_4 with liquid aHCN in the context of their research on uranium cyanides. Besides the position of the IR bands of the obtained compound, only its decomposition to UCl_4 and HCN under vacuum was reported.² These authors synthesized the HCN adduct according to eqn (1) in prospect of the synthesis of uranium cyanides by the elimination of hydrogen chloride from the intermediate compound by addition of a base (eqn (2)), in which they were unsuccessful.

$$UCl_4 + xHCN \rightarrow [UCl_4(HCN)_x]$$
(1)

$$[\mathrm{UCl}_4(\mathrm{HCN})_x] + \mathrm{B} \rightarrow [\mathrm{UCl}_{4-x}(\mathrm{CN})_x] + \mathrm{HB}^+ + \mathrm{Cl}^- (\mathrm{B} = \mathrm{Base})$$
(2)

However, when they reacted UCl_4 with NH_4CN in liquid ammonia, they were able to substitute one chloride ion by a cyanide ion, forming $[UCl_3(CN)] \cdot 4NH_3$. Having reported on the HCN adduct of UF_5 recently,²⁷ we wondered what the nature of the HCN adduct of UCl_4 should be.

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After sublimation of aHCN onto a sample of powdered grassgreen UCl₄, a turquoise colored powder under a colorless liquid was obtained after melting of the HCN. Removing the excess of HCN after one week under cooling led to a highly moisture sensitive blueish green powder of the composition $[UCl_4(HCN)_4]$. The compound is relatively stable at room temperature, if free from residual HCN.

After two weeks of storage at 2 °C under liquid HCN we observed signs of decomposition of the solvent. Namely, a brown tint occurred and flocculation of a brown substance started. So, neither crystallization in HCN nor growing crystals by application of heat was successful, because of the thermal instability of [UCl₄(HCN)₄]. The powder X-ray diffraction pattern obtained at room temperature could be indexed in the tetragonal crystal system and the unit cell parameters could be determined. Mass spectrometry coupled thermal analysis indicated a mass loss of four equivalents of HCN per UCl₄. The IR spectra (see below) indicated U-N bonding as the H-C stretch was observed. A pycnometric density measurement led to approximately $\rho = 2.76 \text{ g cm}^{-3}$ and thus indicated Z = 2. The extinction conditions only pointed to I centering. So, the structure could be solved by crystallographic reasoning. However, only the uranium atom could be refined using the powder X-ray data. The position of the C, Cl, and N atoms could not be located as well as the H atom positions. Using powder neutron diffraction data (Fig. 2), the structure solution and refinement succeeded in the space group $I\bar{4}$ with cell parameters a = 9.0137(2) Å, c = 7.4037(3) Å, V = 601.53(2) Å³, and Z = 2 at T = 295 K, and a = 8.9122(4) Å, c = 7.3255(7) Å, and V = 581.84(7) Å³ at T = 50 K. All atoms could be located and their displacement parameters refined isotropically.

The uranium atom is coordinated by four Cl atoms and by four HCN molecules in a bisphenoidal shape (Fig. 1). The HCN molecules coordinate *via* the N atom to the U atom, as

Table 1 Assignment of IR bands of $[UCl_4(HCN)_4]$, solid,³⁴ and gaseous HCN.³⁵ Numbering according to the literature³⁵

$[\text{UCl}_4(\text{HCN})_4]$ $\tilde{\nu}/\text{cm}^{-1}$	$\mathrm{HCN}(\mathrm{gas})$ $\tilde{\nu}/\mathrm{cm}^{-1}$	$\frac{\text{HCN}(\text{solid})}{\tilde{\nu}/\text{cm}^{-1}}$	Assignment
3159	3311	3132	ν ₃ : ν(C-H)
2119	2097	2097	$\nu_1: \nu(C \equiv N)$
785	712	838	$\nu_2: \delta(H-C \equiv N)$
762		828	$\nu_2: \delta(H-C \equiv N)$

expected. The U-Cl distance is observed to be 2.623(9) Å, the U–N distance to be 2.603(8) Å. Both are in the range of atomic distances reported for other compounds of bisphenoidal shape, such as the analogous acetonitrile complex [UCl₄(CH₃CN)₄] (U-Cl: 2.620(4)-2.627(4),²⁸ resp. 2.614(2)-2.624(2) Å,²⁹ U-N: 2.577(14)-2.601(13),²⁸ resp. 2.567(6)-2.599(6) Å²⁹) which however does not crystallize isotypically, or in the bipyridine complex $[UCl_4(Me_2bpy)_2]$ (U-Cl: 2.622(2)-2.641(1) Å, U-N: 2.617(3)-2.674(3) Å).³⁰ As opposed to these reports the U-N distance is longer in the amine complex, [UCl₄(1,2-bis(dimethylamino)ethane)₂], which is likely due to steric reasons (U-Cl: 2.600(4)-2.617(3) Å, U-N: 2.769(9)-2.810(8) Å).³¹ The molecular structure is quite similar as well to the nitrile adducts reported in the literature.^{45,46} Finally, the uranium(\square) complex [UCl₃(pyridine)₄]₂ shows slightly longer U-N as well as U-Cl_{terminal} atomic distances (U-Cl: 2.734(2)-2.768(2) Å, U-N: 2.690(8)-2.772(7) Å) as may be expected.³² The N-C bond length observed by us is 1.13(1) Å, the C-H bond length is 1.05(3) Å. Both bond lengths are the same as those of pure HCN within the three sigma criterion when compared to atomic distances obtained from the microwave spectroscopic data of gaseous HCN (C-N: 1.156(1) Å, C-H: 1.064(4) Å),³³ as well as for estimations of bond lengths for solid HCN with reference to X-ray and IR spectroscopic data (C-H: 1.07(2) Å, C-N: 1.160(5) Å).^{21,34} This observation is in accordance with other HCN coordination



Fig. 2 Neutron diffraction pattern of $[UCl_4(HCN)_4]$ at 50 K: experimental data (black crosses), calculated Rietveld profile (red) and difference profile (bottom, black). The calculated reflection positions are shown as black ticks. The range from 0 to *ca*. 7° 2 θ has been excluded from the refinement.



Fig. 3 Molar susceptibility and effective magnetic moment of $[UCl_4(HCN)_{4'}]$.

compounds like $[TiCl_4(HCN)_2]$ (C–N: 1.11(1) Å),¹⁰ $[NbCl_5(HCN)]$ (C–N: 1.090(4) Å),²² and $[VCl_4(NCH)_2]$ (C–N: 1.12(1)–1.14(1) Å, C–H: 1.11(9) Å).²³ In the IR spectrum of the title compound (Fig. S1, ESI†) we observed bands at 3159, 2119, 785, and 762 cm⁻¹ which correspond well to the reported ones (3150, 2115, 785 and 760 cm⁻¹).² For their assignment see Table 1. The bands are only slightly shifted compared to gaseous HCN (3311, 2097, and 712 cm⁻¹).³⁵ We undertook an attempt to obtain Raman spectra but despite several attenuations of the laser beam only sample decomposition was observed.

As reported,² HCN can be removed from $[UCl_4(HCN)_4]$ by the application of fine vacuum whereby pure UCl_4 is recovered. At atmospheric pressure, thermal decomposition occurs significantly between 70 and 150 °C. In this range, a mass loss of approximately 19% (22.16% in theory) was detected that was assigned to HCN *via* simultaneous mass spectrometry of the liberated gas. The deviation between the observed and calculated mass loss is ascribed to the transfer of the sample into the thermogravimetric analysis instrument in air and subsequent evacuation and purging of the device. This handling may cause partial hydrolysis and loss of some HCN in the vacuum.

A color change to a more greenish color was visible after storing the compound in a vanadium cuvette for one year. Powder X-ray diffraction hints to the presence of a tiny amount of UCl₄. We attribute this to the decomposition of the compound due to its slight HCN vapor pressure even at room temperature. In closed vessels, HCN would be continuously removed from the gas phase due to its polymerization.

Investigation of the magnetic properties of the compound with a physical property measurement system shows an almost temperature independent susceptibility in the range from 1.8 K to 80 K. Above this range it changes to a Curie-like paramagnetic behavior. Fig. 3 shows the molar susceptibility as well as the effective magnetic moment in number of Bohr magnetons per formula unit. The value at 300 K is 3.0 BM f.u.⁻¹.

Fig. 4 shows the data of the temperature dependent scan in different representations as well as the corresponding Curie–Weiss-fitting curves. The fitting results should be regarded as a rough approximation. The Curie–Weiss fits were performed in a range from 200 to 300 K as we assume that the magnetic properties agree better with a Curie-like behavior in this temperature range.



Fig. 4 Temperature dependent scan at 0.1 T and fitting (red).

The resulting values are 3.82 BM f.u.⁻¹ for the effective magnetic moment ($n_{\rm eff}$), and -181 K for the Weiss constant. The Weiss constant does not indicate an antiferromagnetic interaction between the uranium($_{\rm IV}$) ions. It can be interpreted as a parameter that compensates for the overestimated $n_{\rm eff}$ value.

The temperature-independent part as well as the deviation of the susceptibility from the Curie-law gives reason to a more complex view. For several uranium(w) compounds similar magnetic properties were reported.^{36–38} An admixture of excited states to the ³H₄ ground-state depends naturally on the influence of the ligands due to the orbital overlap.^{47,48} These phenomena seem to be responsible for the observed behavior of the compound.

In conclusion, $[UCl_4(HCN)_4]$, which is only the second example of a hydrogen cyanide complex of a uranium compound, has been synthesized and structurally characterized by a combination of powder neutron and X-ray diffraction, as well as IR spectroscopic, magnetic and thermal analyses. The paramagnetic compound crystallizes in the tetragonal space group $I\overline{4}$. It loses HCN upon heating to 100 °C or in a vacuum at room temperature, whereby UCl₄ is recovered. Such compounds may be useful for the chemical vapor deposition of nitride films and potentially for the formation of uranium nitrides. Investigations are ongoing.

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Conflicts of interest

None to declare.

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