Supporting information

**[UCl\(_4\)(HCN)\(_4\)] – A hydrogen cyanide complex of uranium tetrachloride**

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**Experimental Procedures**

*Caution:* Hydrogen cyanide is a highly toxic liquid with a boiling point of 26 °C. It can only be smelled by a fraction of people.\(^39\) Use of electronic detector systems is recommended. Working in fume hoods and closed apparatuses is obligatory. HCN should be stabilized for storage by a suitable substance like P\(_2\)O\(_5\) and handled in acid treated vessels to prevent polymerization.\(^39\)

All work was carried out in flame dried borosilicate glass under inert conditions in an atmosphere of dried and purified argon (5.0, Praxair) using Schlenk technique or a glovebox (MBraun). Glassware for the handling of HCN was pretreated with 1% H\(_2\)SO\(_4\) for several hours to acidify the surface.\(^39\) PTFE grease (Carl Roth) proved to be superior to Kel-F grease which was dissolved by HCN.

KCN (p.A. Merck KGaA) was used as supplied. UCl\(_4\) was synthesized by the reaction of UO\(_2\) with AlCl\(_3\) and purified by chemical vapour transport.\(^40\)

**Synthesis of HCN:** A solution of 83 g KCN (1.27 mol, 1 eq.) in 200 ml H\(_2\)O was slowly (1 h) dropped into a solution of 136 ml H\(_2\)SO\(_4\) (96 %, 74.1 g, 0.73 mmol, 3.4 eq.) in 100 ml H\(_2\)O to which 2.5 g FeSO\(_4\)∙7H\(_2\)O (9 mmol) were added.\(^41\) The evolving gas was expelled by careful heating with an oil bath. The starting temperature of the bath of 80 °C was slowly risen to 115 °C towards the end of the distillation (after 2 h). The gas passed over a 20 cm Vigreux column through a Liebig condenser into a trap at 50 °C that contained some boiling-chips. A U-tube filled with CaCl\(_2\) granules was connected to this trap and was also kept at 50 °C. Finally, the gas was condensed in a Liebig condenser cooled to −10 °C (cryostat) and collected as a colourless solid in a J-Young valve round bottom flask, which was cooled with a NaCl/ice cooling bath. The flask was filled with approximately 2 g of Sicapent (Merck). Exhaust gasses were led through a CaCl\(_2\) filled column and two gas washing bottles, the last one filled with 115 ml of 50 % KOH solution. A mercury pressure-relief valve connected to the first Liebig condenser prevented pressure build up in case of clogging. For further purification, the raw HCN (27.5 g, 40 ml, 1.0 mol, 80 % yield) was refluxed over Sicapent for 2 hours and sublimed onto fresh Sicapent for storage. The yield was 25.0 g (36 ml, 0.93 mol, 73 % of theory based on KCN).

**Synthesis of [UCl\(_4\)(HCN)\(_4\)]:** With the help of a dry ice cooling bath, 4.0 g of HCN (148.0 mmol, 5.8 ml, 1.04 eq.) were sublimed onto 3.5 g of finely ground UCl\(_4\) (35.5 mmol, 1 eq.). Upon melting of the HCN, the grass green UCl\(_4\) immediately started to expand in volume and changed its colour to a light turquoise green. After one night, the reaction was complete and almost no liquid was left in the reaction vessel. After six days at 2 °C the excess HCN was removed by sublimation with the help of a dry ice isopropanol bath, while the product was cooled with ice. Last residues of free HCN were expelled with a slight stream of argon. Evacuation of the vessel must be avoided. The yield is quantitative. A longer storage under liquid HCN led to slow formation of brown polymers of HCN.

**Powder X-ray diffraction:**

Powder X-ray diffraction was conducted at room temperature with a STOE Stadi MP powder diffractometer using Cu-K\(_\alpha\) radiation, a Ge monochromator and a Mythen1K detector. The sample was ground in the reaction vessel with a flame-dried glass pestle and filled into a 0.3 mm capillairie attached to a side joint of the reaction vessel.

Le Bail fitting was carried out with JANA 2006.\(^42\)

**Powder neutron diffraction:**

Powder neutron diffraction patterns were recorded in an indium-sealed vanadium cuvette of 10 mm diameter at 300 and 50 K by using the SPODI neutron powder diffractometer (λ = 1.54830 Å) at the research reactor FRM II.\(^43\) The cuvette was filled to approximately 75 % filling level with 4 g of [UCl\(_4\)(HCN)\(_4\)] using Schlenk technique.

Le Bail fitting and structure refinement was carried out with JANA 2006.\(^42\) The 2θ interval from 0 to 7.54° was excluded from the refinement. Refinement was carried out on \(^F^2\) and converged at \(R\)(all) = 3.94, \(wR^2\) = 4.12 (GoF = 1.81, \(R_P\) = 3.14, \(wR_P\) = 3.55). The background was refined using a manual background. The Pseudo-Voigt function (GU, GV, LX) was used to model the reflection profiles, the lattice parameters \(a\) and \(c\) were refined. All atoms were refined isotropically, an anisotropic refinement was unfortunately not possible.

**Thermal analysis:**

Thermal gravimetric analysis was carried out by using a Netzsch STA 409C instrument equipped with a TASC 414/3 signal amplifier and a Pfeiffer Omnistar GSD 301 O mass selective analyser. [UCl\(_4\)(HCN)\(_4\)] was heated to 500 °C at a rate of 10 K min\(^{-1}\) in a corundum crucible.
Additionally, 526.6 mg of $[\text{UCl}_4(\text{HCN})_4]$ were placed in a glass vial inside a Schlenk tube and evacuated to a constant pressure of $1 \cdot 10^{-3}$ mbar for five days. 413.4 mg of phase pure UCl$_4$, as evidenced by powder X-ray diffraction, were recovered, representing a mass loss of 21.5% (calc.: 22.2%).

IR- and Raman-spectroscopy:

IR-spectra were recorded with a Bruker alpha FT-IR spectrometer using a Germanium ATR unit with a resolution of 4 cm$^{-1}$ inside a glovebox. Spectra were processed with the OPUS software package. Raman spectra were recorded with a HORIBA Jobin Yvon’s LabRAM 800HR spectrometer, using the 632.832 nm excitation line of a He/Ne laser. A sample of $[\text{UCl}_4(\text{HCN})_4]$ was sealed inside a 0.3 mm borosilicate glass capillary, which was flame dried before use. The sample decomposed in the laser beam and no spectrum could be recorded. Several attenuations also did not lead to success.

Magnetic properties

DC-magnetic data of UCl$_4$(HCN)$_4$ were collected with the aid of the VMS option of a physical property measurement system (LOT/QD Darmstadt). Temperature dependent magnetic data were recorded. A temperature dependent scan from 1.8 K to 300 K was taken with an applied magnetic field of 0.1 T. The collected data were corrected with respect to the diamagnetic moment of the sample holder, as well as to the diamagnetic contribution ($\chi_{\text{dia}} = -1.285 \cdot 10^{-4}$ cm$^3$ mol$^{-1}$) of the sample derived from Pascal constants. The result is the net paramagnetic data.