Supporting Information for:

Well-Defined Molecular Uranium (III) Chloride Complexes

*Henry S. La Pierre, Frank W. Heinemann, and Karsten Meyer**

Inorganic Chemistry, Department of Chemistry and Pharmacy, Friedrich-Alexander-University of Erlangen-Nuremberg, Egerlandstrasse 1, 91058 Erlangen, Germany

* Corresponding author's email address: karsten.meyer@fau.de

Supporting Information Table of Contents

General Considerations

All air- and moisture-sensitive experiments were performed under dry nitrogen atmosphere using standard Schlenk techniques or in MBraun inert-gas glovebox containing an atmosphere of purified dinitrogen. The glovebox is equipped with a -35 °C freezer. Solvents were purified using a two-column solid-state purification system (Glass Contour System, Irvine, CA), transferred to the glovebox without exposure to air, and stored over molecular sieves and sodium (where appropriate). All glassware was dried by storage in an oven overnight (> 8 h) at a temperature > 160 ºC. Celite was dried in an oven for a minimum of 3 d at a temperature > 160 ºC. NMR solvents were obtained packaged under argon and stored over activated molecular sieves and sodium (where appropriate) prior to use. [UCl_4] was prepared according to literature procedures.[1] All other reagents were acquired from commercial sources and used as received. Mg turnings were activated by heating under vacuum with a heat gun 7 times with vigorous magnetic stirring.

^1H NMR spectra were recorded on a JEOL ECX 400 instrument at a probe temperature of 23 °C. Chemical shifts, δ, are reported relative to residual ^1H resonances of the solvent in ppm. Electronic absorption spectra were recorded from 250 to 2200 nm (Shimadzu, UV-3600) in the indicated solvent at room temperature. Infrared (IR) spectra were recorded on a Shimadzu Affinity-1 CE FTIR instrument from 400 to 4000 cm^{-1}. Solid samples of the compounds were homogenized with excess amount of KBr and a pressed pellet was measured at room temperature. Elemental analyses were obtained using Euro EA 3000 (Euro Vector) and EA 1108 (Carlo-Erba) elemental analyzers in the Chair of Inorganic Chemistry at the University Erlangen-Nuremberg (Erlangen, Germany).

Synthetic Procedures

Synthesis of [$UCl_3(py)_4]_2$ (1).

Method A – large scale: To an oven dried 500 mL Teflon tapped Schlenk flask was added 2.00 g of Mg turnings and a large Teflon stir bar. The flask was cooled under vacuum and then Mg turnings were mechanically activated through 7 heating cycles (by heat gun) with rapid magnetic stirring under vacuum. The flask was then cooled to room temperature, sealed, and transferred to the glove box. It was further charged with [UCl_4] (4.00 g, 10.5 mmol) and 60 mL of 1,4-dioxane. On the addition of solvent, the slurry formed a green/grey block including in the stir bar. The sealed flask was removed from the box and sonicated with occasional shaking for 1 h, after which time a fine grey/white suspension had formed and the stir bar had been liberated. The sealed flask was then heated in an oil bath at 100 °C for 3 d (72 h), after which it was cooled to room temperature. During the course of the reaction a fine blue precipitate formed (see photo below). The flask was returned to the glove box and the blue suspension was decanted off the remaining Mg turnings and onto a glass frit and washed with (2 x 50 ml) 1,4-dioxane. The remaining volatiles were removed *in vacuo* from the residue on the frit. Following extraction of the residue into pyridine (250 mL) and filtration through a fine porosity glass frit, hexane (350 mL) is added slowly to the solution (in a 1 L round bottom flask) with magnetic stirring. After the addition of hexane is complete, stirring is stopped and the solution allowed to stand for 10 min., during which time fine purple/–black crystals precipitate. The microcrystalline material is isolated on a frit, washed with 50 mL of hexane, and remaining volatiles are removed *in vacuo* to give the title complex (with loss of pyridine since it is vacuum sensitive) in 72 % yield (based on U) for [U_2Cl_6•7.4(Py)]. Elemental analysis for $Cl_6U_2 \bullet 7.4\ C_5H_5N$, calc'd C 34.88, H 2.93, N 8.13; found C 34.99, H 2.84, N 7.92.

Method B – box scale: To 20 mL scintillation vial charged with [UCl_4] (400 mg, 1.05 mmol), activated Mg turnings (200 mg), and a Teflon coated stir bar was added 10 ml of 1,4-dioxane. The slurry was heated to 90 °C for 3 d (72 h), after which it was allowed to cool to room temperature with continued stirring. The blue suspension was decanted off the remaining Mg turnings onto a glass frit and washed with (2 x 5 ml) 1,4-dioxane. The remaining volatiles were removed *in vacuo* from the residue on the frit. Elemental analysis of this residue suggests the expected formulation $[UCl_3(1,4\text{-dioxane})_2]_2 \bullet [MgCl_2(1,4\text{-dioxane})_2]$. Calc'd for $C_{24}H_{48}Cl_8MgO_{12}U_2$: C 21.96, H 3.96; Found: C 21.59, H 3.58. Following extraction of the residue into pyridine (25 mL) and filtration through a fine porosity glass frit, hexane (35 mL) is added slowly to the solution with magnetic stirring. After the addition of hexane is complete, stirring is stopped and the solution allowed to stand for 10 min. during which time fine purple/black crystals precipitate. The microcrystalline material is isolated on a frit, washed with 5 mL of hexane, and remaining volatiles were removed *in vacuo* to give the title complex in 41% yield (285 mg, 0.22 mmol).

Elemental analysis for $C_{40}H_{40}N_8Cl_6U_2$, calc'd C 36.35, H 3.05, N 8.48; found C 37.05, H 3.10, N 8.38. IR (cm^{-1}): 3369 (br m), 3064 (m), 1627 (w), 1599 (s), 1485 (m), 1440 (s), 1220 (m), 1151 (w), 1066 (m), 1037 (m), 1004 (m), 756 (m), 700 (s), 675 (w), 623 (m), 422 (w). ^1H NMR (Py-d_5, 399.78 MHz): 4.4 equivalents of Py-h_5 per U (12.0 mg $[UCl_3(py)_4]_2$ and 3.6 mg hexamethylbenzene gives *para*-Py to HMB integral ratio of 1:4.08).

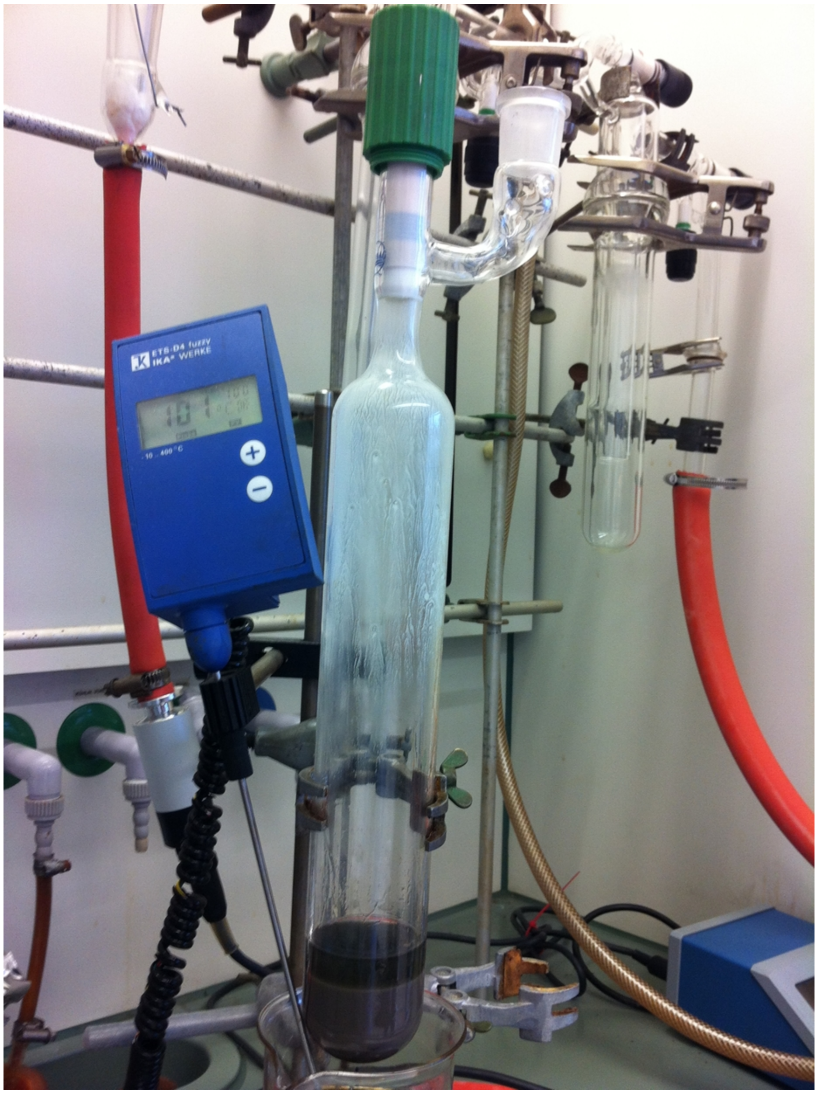
Recrystallization by diffusion of diethyl ether into pyridine at –35 °C gives X-ray quality crystals of **1 • 4 C_5H_5N**.

Synthesis of $[(N(Me_3Si)_2)_3U(py)]$. To a slurry of **1** (prepared by method B) (200 mg, 0.15 mmol, 1.0 equivalent) in 2 mL of tetrahydrofuran was added $NaN(Me_3Si)_2$ (160 mg, 0.91 mmol, 6.0 equivalents) in 3 mL tetrahydrofuran. The reaction mixture was stirred for 4 h and then reduced to a residue *in vacuo*. After extraction with 5 ml pentane, the solution was filtered through Celite and again reduced to a residue *in vacuo* to give the title compound in 78 % yield (185 mg, 0.23 mmol) as a red/purple powder. The proton NMR collected in C_6D_6 was consistent with previously reported data (pyridine resonances are broadened into baseline).[2]

^1H NMR (C_6D_6, 399.78 MHz): –7.55 (s, 54 H).

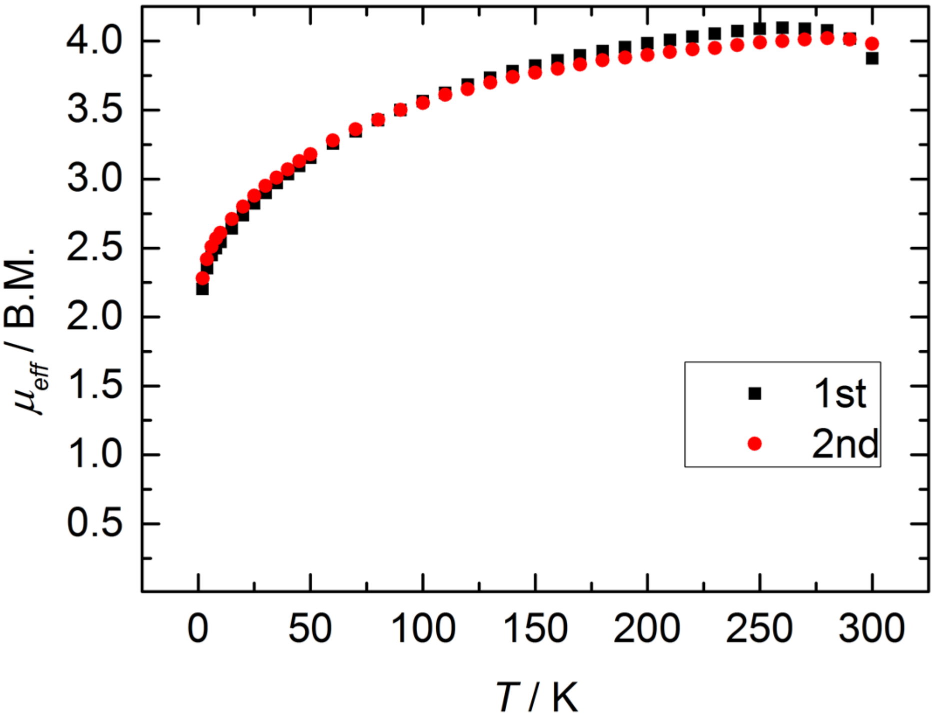
Synthesis of [UCl(py)$_4$(μ-Cl)$_3$U(py)$_2$(μ-Cl)$_3$UCl$_2$(py)$_3$] (2). Diffusion of hexane into a solution of **1** in pyridine at room temperature over the course of 3-5 days gives **2** as X-ray quality plates. Occasionally a white precipitate forms first – presumably [MgCl$_2$(py)$_2$]. Decantation and resumption of hexane diffusion gives the title complex. Elemental analysis for $C_{45}H_{45}Cl_9N_9U_3$, calc'd C 30.97, H 2.60, N 7.22; found C 31.51, H 2.64, N 7.08.

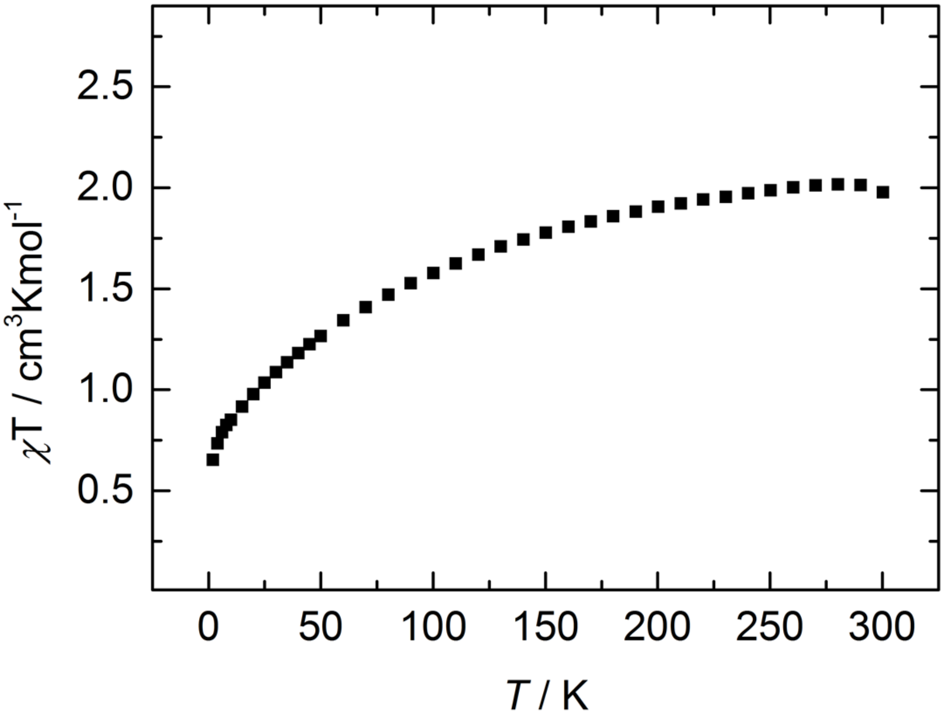
Photo of 500 mL flask after 24 h from Method A:

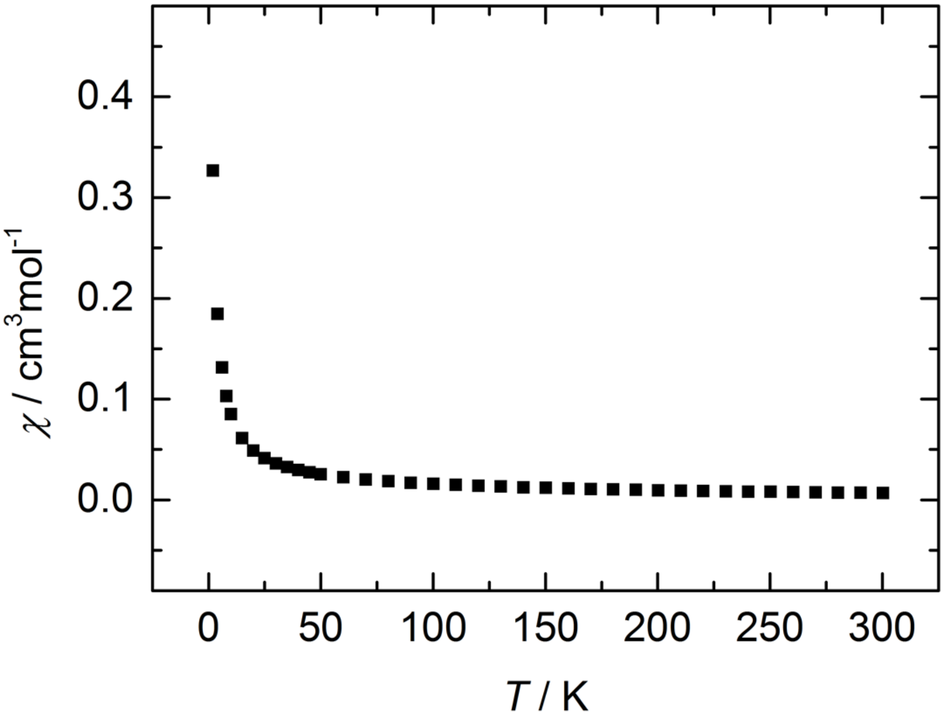


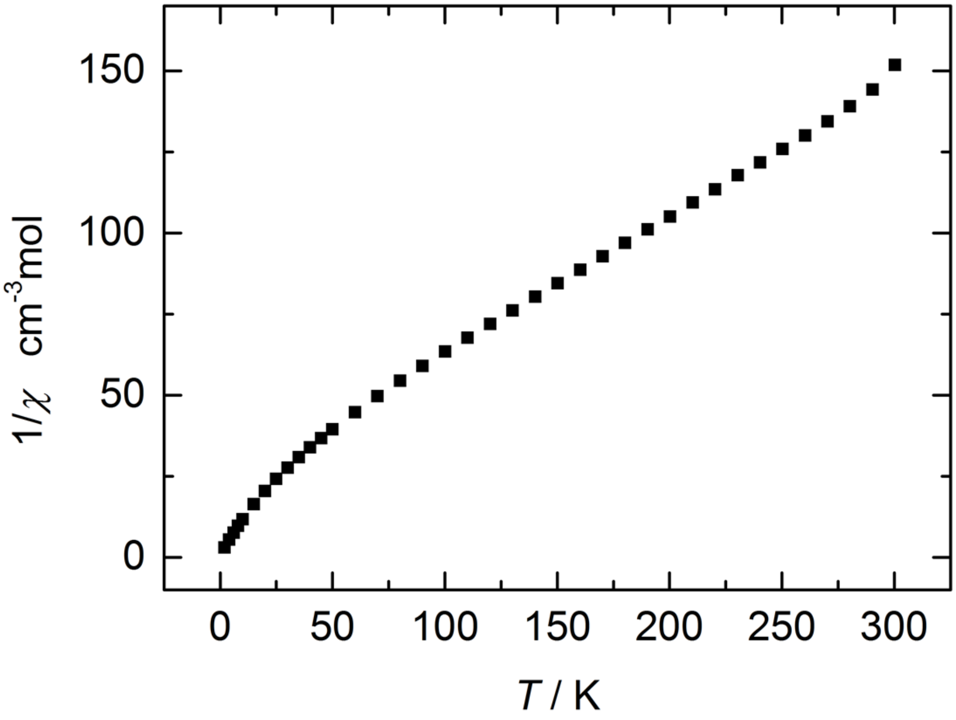
SQUID Magnetization Studies

SQUID magnetization data of powdered samples were recorded with a SQUID magnetometer (Quantum Design) at 10 kOe between 2 and 300 K for all samples. Values of the magnetic susceptibility were corrected for the underlying diamagnetic increment by using tabulated Pascal constants and the effect of the blank sample holders (gelatin capsule/straw). Diamagnetic corrections (χ_{dia} [10^{-6} cm^3 mol^{-1}]) used for the complex **1** is (–624.40) and is reported for the formula unit (*i.e.* for the dimer). Samples used for magnetization measurement were checked for chemical composition and purity by elemental analysis (C, H, and N). Data reproducibility was also checked by obtaining data on two independently synthesized samples.




χT / cm^{3}Kmol^{-1}
2.5
2.0
1.5
1.0
0.5
0
50
100
150
200
250
300
T / K


χ / cm^{3}mol^{-1}
0.4
0.3
0.2
0.1
0.0
0
50
100
150
200
250
300
T / K



1/χ cm^-3 mol
0
50
100
150
0
50
100
150
200
250
300
T / K

X-ray Crystallography

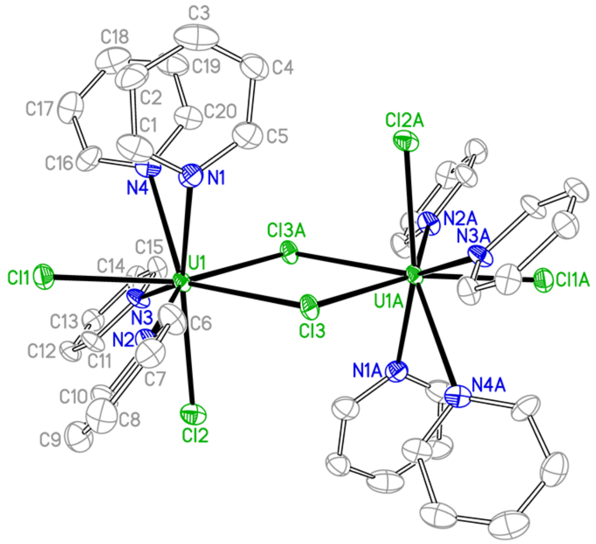
CCDC-**976568** (for **1**) and CCDC-**976569** (for **2**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/products/csd/request/ (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK. fax: ++44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Crystallographic Details. Crystals of **1** and **2** were coated with isobutylene oil on a microscope slide. Intensity data were collected using MoKα radiation (λ = 0.71073 Å) either at 100 K on a Bruker SMART APEX II diffractometer. Data were corrected for Lorentz and polarization effects, semi-empirical absorption corrections were performed on the basis of multiple scans using SADABS[3] for **2** and TWINABS for **1**.[4] All structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 using SHELXTL NT 6.12.[5]

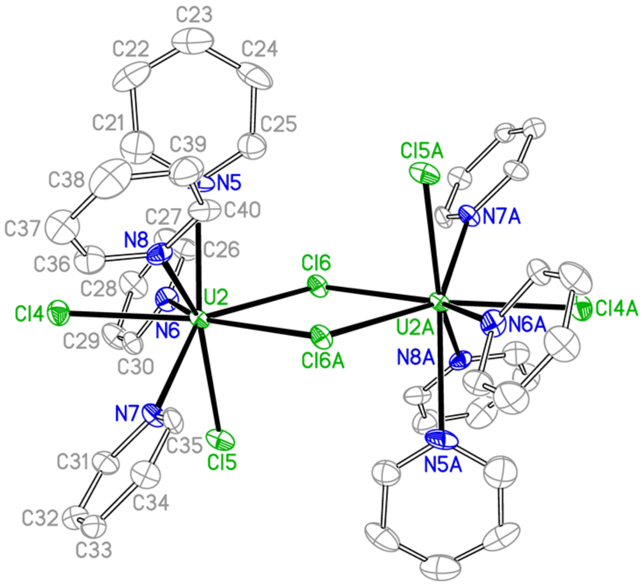
Compound 1. All non-hydrogen atoms were refined anisotropically. A large number of crystals were investigated, all suffered from twinning (split crystals). Best results were obtained for this crystal using a detwinned HKLF 4 file. Remaining positive and negative non-metal residual electron density might result from the fact that not all domains of the split crystal could be properly treated so that artefacts persist. The asymmetric unit contains two halves of the dinuclear complex with the complex being located on a crystallographic inversion centre in both cases. The compound crystallized with a total of four molecules of pyridine per formula unit. One of the pyridine solvent molecules was disordered. Two alternative orientations were refined with resulting site occupancies of 56(2) and 44(2) % for the atoms, N12, C56 – C60 and N12A, C56A – C60A, respectively. SAME and SIMU restraints were applied in the refinement of the disorder. Treatment of hydrogen atoms: All hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to those of their corresponding carrier atoms by a factor of 1.2 or 1.5.

Compound 2. All non-hydrogen atoms were refined anisotropically. Treatment of hydrogen atoms: All hydrogen atoms were placed in positions of optimized geometry, their isotropic displacement parameters were tied to those of their corresponding carrier atoms by a factor of 1.2 or 1.5.

Molecular structure of **1** in crystals of **1 • 4 C_5H_5N** (first of two independent molecules with the applied numbering scheme, 50 % probability ellipsoids, hydrogen atoms and solvent molecules omitted for clarity):



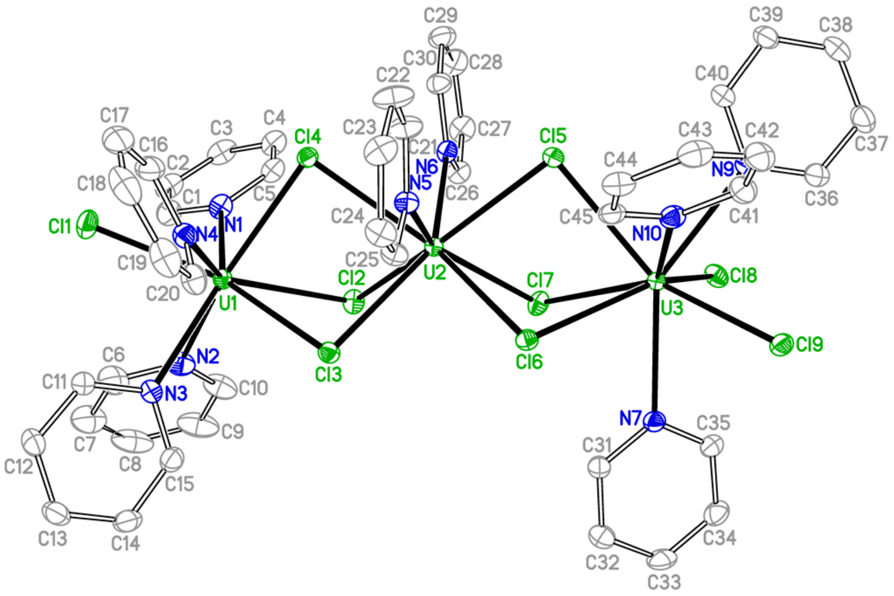
Molecular structure of **1** in crystals of **1 • 4 C_5H_5N** (second of two independent molecules with the applied numbering scheme, 50 % probability ellipsoids, hydrogen atoms and solvent molecules omitted for clarity):



Crystallographic and Refinement Data for 1.

Identification code	hsl1318	
Empirical formula	$C_{60}H_{60}Cl_6N_{12}U_2$	
Formula weight	1637.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 12.4942(9) Å	α = 87.833(4) °
	b = 15.9632(12) Å	β = 89.498(4) °
	c = 16.1661(12) Å	γ = 76.857(4) °
Volume	3137.6(4) $Å^3$	
Z, Calculated density	2, 1.734 Mg/m^3	
Absorption coefficient	5.458 mm^{-1}	
F(000)	1580	
Crystal size	0.55 x 0.40 x 0.05 mm	
Theta range for data collection	2.10 to 27.00 °	
Limiting indices	$-15<=h<=15$, $-20<=k<=20$, $0<=l<=20$	
Reflections collected / unique	115576 / 13688 [R(int) = 0.0929]	
Completeness to theta = 27.00	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.564 and 0.301	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	13688 / 198 / 776	
Goodness-of-fit on F^2	1.319	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0587, wR_2 = 0.1577	
R indices (all data)	R_1 = 0.0758, wR_2 = 0.1634	
Largest diff. peak and hole	2.901 and -2.374 $e.A^{-3}$	

Molecular structure of **2** with the applied numbering scheme (50 % probability ellipsoids, hydrogen atoms and solvent molecules omitted for clarity):



Crystallographic and Refinement Data for 2.

Identification code	hsl1316	
Empirical formula	$C_{45}H_{45}Cl_9N_9U_3$	
Formula weight	1745.04	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 9.323(3) Å	α = 83.534(5) °
	b = 15.877(5) Å	β = 86.604(5) °
	c = 18.916(6) Å	γ = 79.746(5) °
Volume	2735.4(14) Å^3	
Z, Calculated density	2, 2.119 Mg/m^3	
Absorption coefficient	9.339 mm^{-1}	
F(000)	1614	

Crystal size	0.36 x 0.27 x 0.06 mm
Theta range for data collection	2.22 to 29.75 °
Limiting indices	$-13<=h<=12$, $-22<=k<=21$, $-26<=l<=25$
Reflections collected / unique	74540 / 14272 [R(int) = 0.0331]
Completeness to theta = 26.00	99.2 %
Absorption correction	Integration
Max. and min. transmission	0.572 and 0.481
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14272 / 0 / 595
Goodness-of-fit on F^2	1.041
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0200$, $wR_2 = 0.0460$
R indices (all data)	$R_1 = 0.0236$, $wR_2 = 0.0472$
Largest diff. peak and hole	1.578 and -1.073 e.Å^{-3}

References

1. J. L. Kiplinger, D. E. Morris, B. L. Scott and C. J. Burns, *Organometallics*, 2002, **21**, 5978.
2. J. L. Stewart, Ph.D. Thesis, **1988**, University of California, Berkeley, CA.
3. SADABS, Bruker AXS, Inc,, **2009**, Madison, WI, USA
4. TWINABS, Bruker AXS, Inc., **2007**, v. 2007/3, Madison, WI, U.S.A.
5. SHELXTL NT 6.12, Bruker AXS, Inc., **2002**, Madison, WI, USA.