

Electronic Supplementary Information

**UO₂²⁺-Mediated Ring Contraction of Pyrihexaphyrin:
Synthesis of a Contracted Expanded Porphyrin-Uranyl
Complex**

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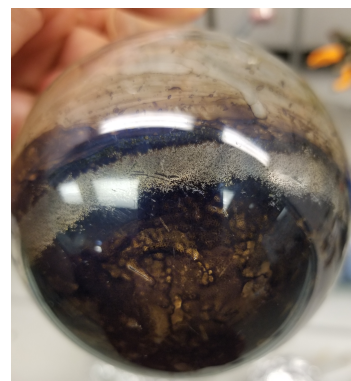
Materials & General Methods

All reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was dried over activated molecular sieves for 48 h and then passed through a short plug of neutral alumina before use. Analytical thin-layer chromatography (TLC) was performed using commercial precoated silica gel plates containing a fluorescent indicator. Column chromatography was carried out using silica gel (0.040-0.063 mm) or basic alumina (aluminum oxide, basic, Brockmann 1, 50-200 μ m, 60A; Acros Organics). High-resolution mass spectra (HRMS) measurements were made using an Ion Spec Fourier Transform mass spectrometer (9.4 T). Proton and carbon NMR spectra were recorded using a Bruker AVANCE III 500 at room temperature. Chemical shifts are reported in ppm using TMS or solvent residual signals as internal reference standards. All NMR spectroscopic solvents were purchased from Cambridge Isotope Laboratories. CDCl_3 utilized for observing intermediate **2** was subjected to three freeze-pump thaw cycles, brought into the box, and stored over 3 Å molecular sieves until use. UV-Vis spectra were recorded from 250 to 800 nm using a Varian Cary 5000 spectrophotometer at room temperature. A cell length of 10 mm was used for all UV-Vis spectral studies. Electrochemical measurements were carried out using anhydrous acetonitrile as the solvent and tetra-*n*-butylammonium perchlorate (TBAOCl_4 , electrochemical grade from Fluka) as the supporting electrolyte. Cyclic voltammetry was carried out with an EG&G model 173 potentiostat/ galvanostat. A three-electrode cell was used consisting of a glassy carbon working electrode, a platinum wire counter electrode, and a silver wire reference electrode. All potentials are reported relative to the ferrocene/ferrocenium couple (Fc/Fc^+), which was used as an external standard to calibrate the reference electrode. Ferrocene was purified by sublimation at 95 °C.

Synthesis and Characterization Data

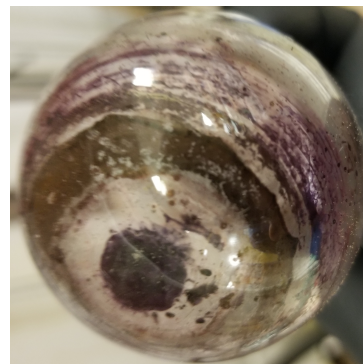
Pyrihexaphyrin (1)

To an oven dried 2 L round bottom flask, 5,5'-(pyridine-2,6-diyl)bis(3,4-diethyl-1*H*-pyrrole-2-carbaldehyde) (**2**) (61 mg, 0.162 mmol) and terpyrrole (**3**) (50 mg, 0.162 mmol) were added and dissolved in CH_2Cl_2 (800 mL). Trifluoroacetic acid (99 μ L) was added and the reaction was stirred open to air at ambient temperature overnight. The reaction mixture was quenched by adding 100 mL of an aqueous 10% NaOH solution. It was then transferred to a separatory funnel and the organic layer separated off. The organic layer was dried over anhydrous MgSO_4 and concentrated *in vacuo*. The resulting solid was subjected to flash chromatography over silica gel (CH_2Cl_2 to 10% acetone/ CH_2Cl_2 , eluent) to yield **1** as a dark yellow solid dominated by a purple metallic hue, as shown in the accompanying photograph. Yield: 85.7% (90 mg). ^1H NMR (500 MHz, chloroform-*d*) δ 10.05 (s, 3H), 7.70 (t, J = 7.8 Hz, 1H), 7.01 (d, J = 7.8 Hz, 2H), 6.57 (s, 2H), 2.70 – 2.38 (m, 12H), 2.12 (s, 6H), 2.02 (s, 6H), 1.18 (dt, J = 14.4, 7.5 Hz, 12H), 1.09 (t, J = 7.5 Hz, 6H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 159.8, 154.1, 146.9, 146.8, 137.2, 136.8, 131.6, 128.5, 127.3, 126.9, 123.9, 122.0, 115.7, 18.3, 17.9, 17.7, 17.4, 16.1, 16.0, 11.9, 11.4. HRMS (ESI⁺) calcd. for $\text{C}_{43}\text{H}_{50}\text{N}_6$ ($\text{M}+\text{H}^+$) 651.4170, found 651.4161.



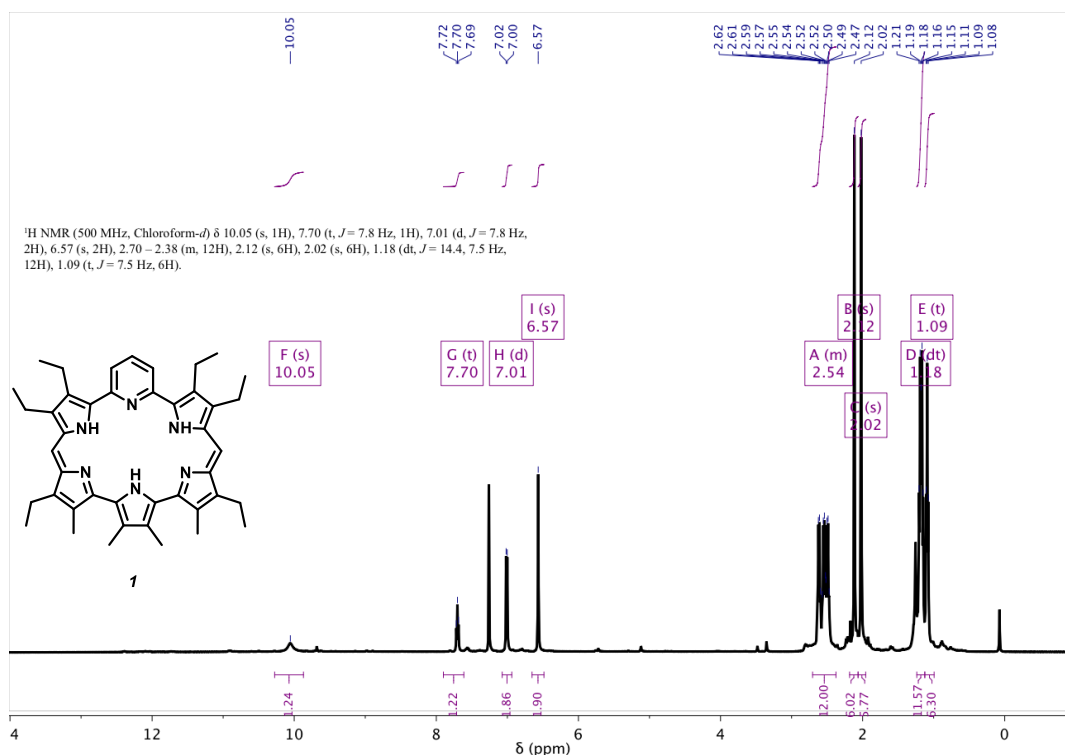
Contracted Pyrihexaphyrin-Uranyl Complex (**4**)

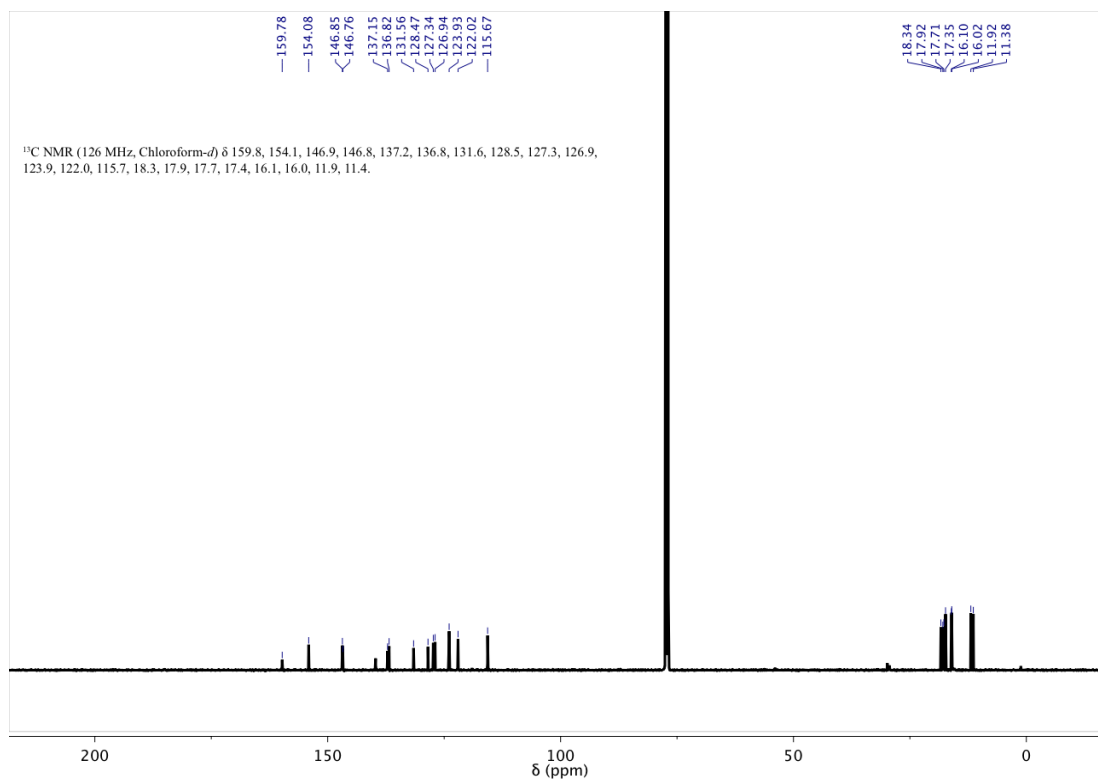
In an inert atmosphere glove box, $\text{UO}_2[\text{N}(\text{SiMe}_3)_2]_2 \cdot 2(\text{THF})$ (68.4 mg, 0.093 mmol) was added to a stirred solution of macrocycle **1** (20 mg, 0.031 mmol) in 5 mL of dry THF. The mixture was stirred at room temperature overnight (ca. 12 h). The reaction mixture was removed from the inert atmosphere glove box and concentrated *in vacuo*. The residue was purified by basic alumina (Al_2O_3) chromatography (eluent, CH_2Cl_2) on the bench top to yield **4** as a dark purple solid with a bronze metallic luster, as shown in the accompanying photograph. Yield: 63-65% (17.7 - 18.3 mg). ^1H NMR (500 MHz, chloroform-*d*) δ 9.67 (dd, $J = 31.5$, 7.7 Hz, 2H), 8.94 (t, $J = 7.8$ Hz, 1H), 8.83 (s, 1H), 3.79 – 3.37 (m, 12H), 3.13 (s, 3H), 3.06 (s, 3H), 3.01 (d, $J = 8.4$ Hz, 6H), 1.81 – 1.55 (m, 18H). ^{13}C NMR (126 MHz, chloroform-*d*) δ 160.3, 157.5, 156.8, 155.1, 154.3, 151.0, 148.2, 148.1, 147.3, 146.9, 145.0, 142.9, 141.9, 141.2, 138.7, 138.1, 136.4, 135.0, 134.7, 134.4, 133.4, 127.7, 120.6, 120.4, 120.0, 19.6, 19.4, 19.2, 18.9, 18.2, 18.2, 17.2, 17.1, 16.7, 16.3, 16.1, 15.1, 14.3, 14.0, 13.6, 13.4. HRMS (ESI⁺) calcd. for $\text{C}_{43}\text{H}_{47}\text{N}_6\text{O}_2\text{U}$ ($\text{M}+\text{H}^+$) 917.4263, found 931.4270.



NMR Spectral & HRMS-ESI Data

Pyrihexaphyrin (**1**)



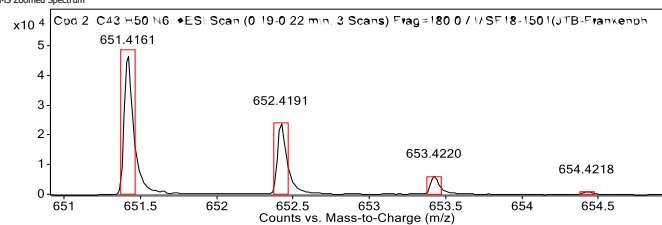


Target Compound Screening Report

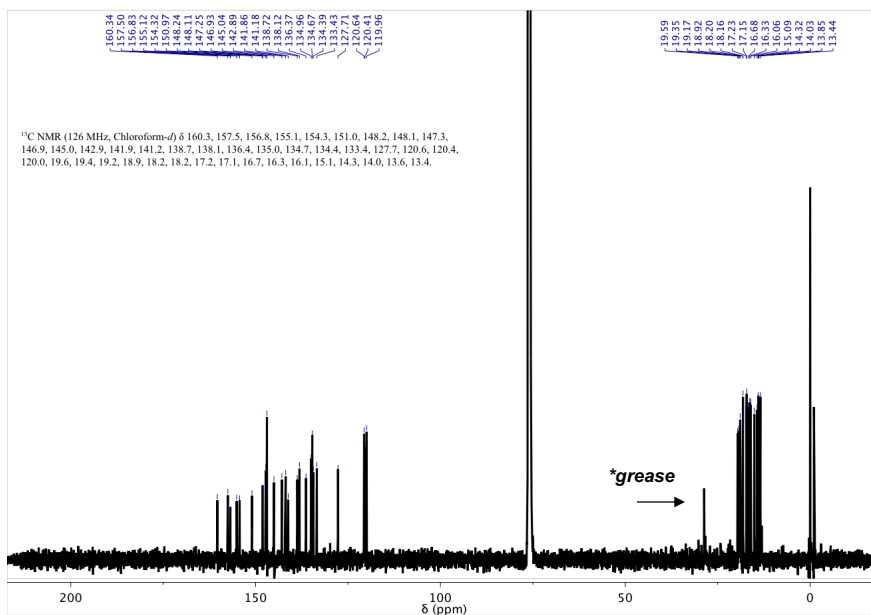
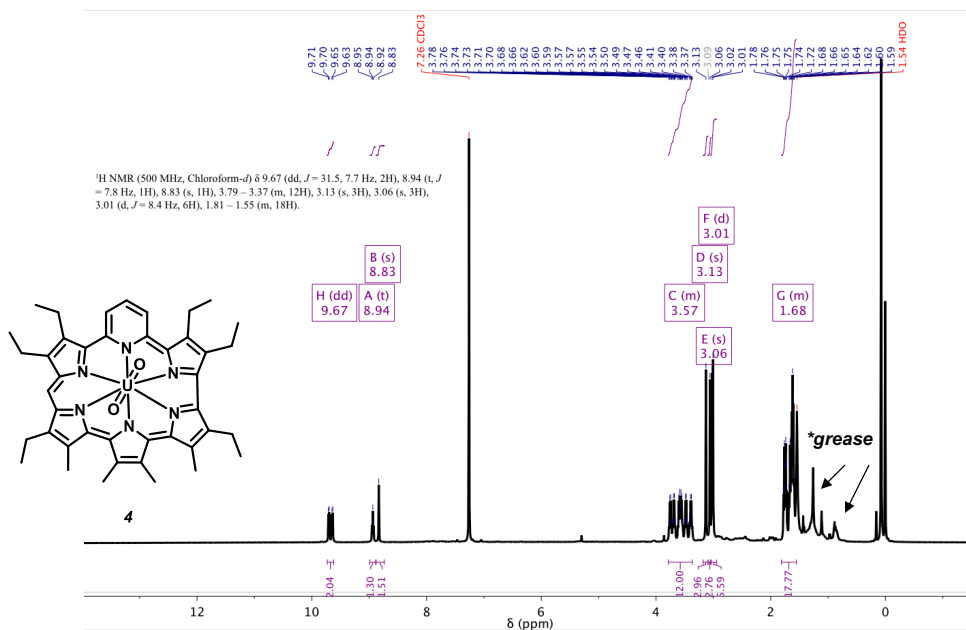
Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

Data File	MSF18-1501(JTB-Frankenphyrin)_hrESIspos2.d	Sample Name	1501(JTB-Frankenphyrin)	Comment	1501(JTB-Frankenphyrin)
Position	P1-C8	Instrument Name	Instrument 1	User Name	
Acq Method	pos.m	Acquired Time	11/1/2018 10:52:39 AM	DA Method	KS.m

MS Zoomed Spectrum



Contracted Pyrihexaphyrin-Uranyl Complex (4)

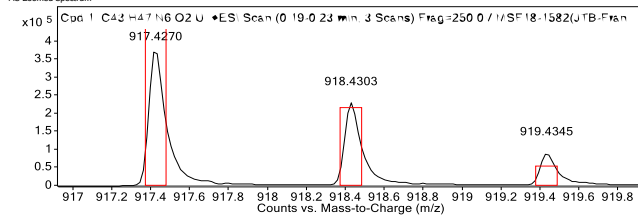


Target Compound Screening Report

Results Acquired by The University of Texas at Austin Mass Spectrometry Facility

Data File	MSF18-1582(JTB-FrankenpyrinUO2)_hrES[post2.d	Sample Name	1582(JTB-FrankenpyrinUO2)	Comment	1582(JTB-FrankenpyrinUO2)
Position	P1-ES	Instrument Name	Instrument 1	User Name	
Acq Method	pos.m	Acquired Time	11/14/2018 1:40:19 PM	DA Method	KS.m

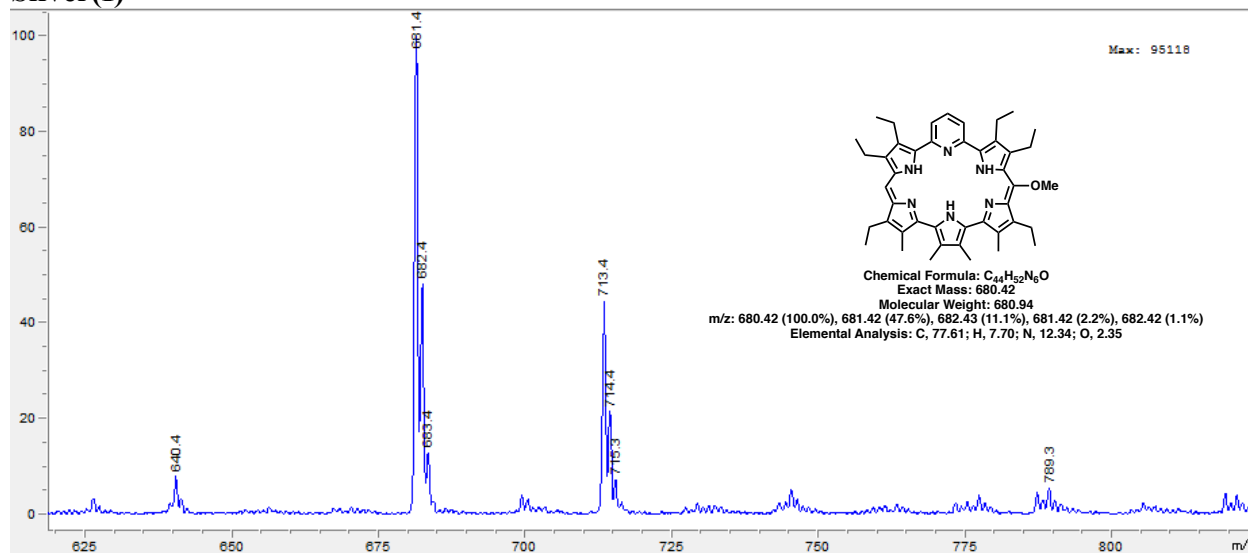
MS Zoomed Spectrum



Low-Res MS analyses of attempts to prepare metallo-pyrrihexaphyrin complexes

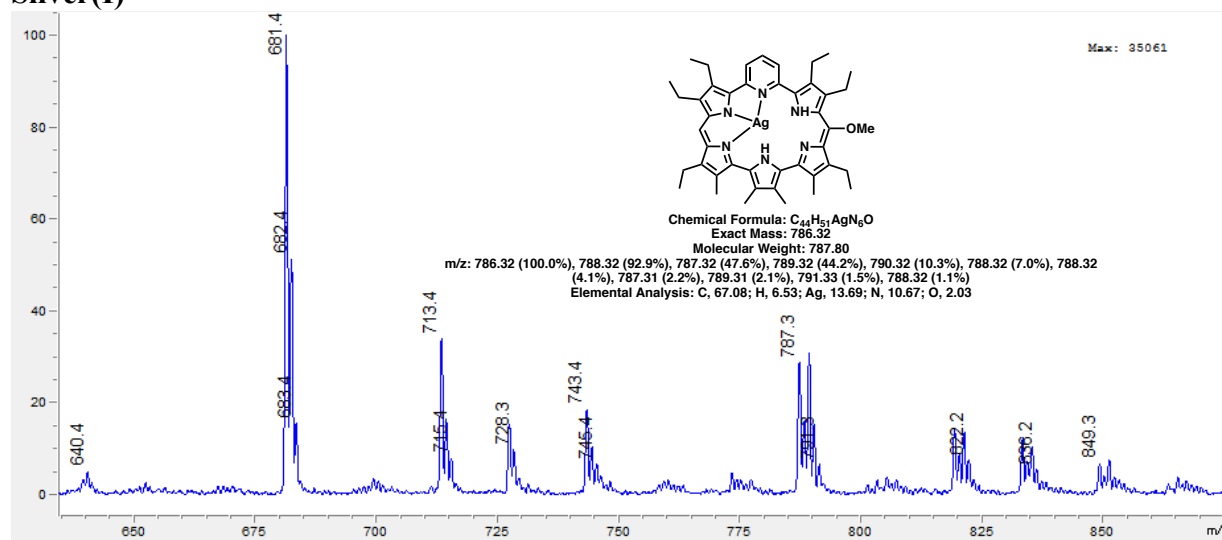
Metalation of **1** was attempted by mixing **1** (1 mg) with various metal cation salts (10 mg) in a mixture of MeOH in CH₂Cl₂ (2 mL, 1:1, v/v), followed by stirring at room temperature for 24 hours. The reaction samples were then dried under a stream of N₂, dissolved in CH₂Cl₂, and passed through a basic alumina glass pipette plug using acetone as the eluent. Putative products were subjected to mass spectrometric (ESI) analysis. As noted in the main text, the following salts were tested: AgOAc, Cu(OAc)₂, Co(OAc)₂, Fe(OAc)₂, In(OAc)₃, ZrCl₄, Ni(OAc)₂, Gd(OAc)₃, and VO(acac)₂.

Silver(I)



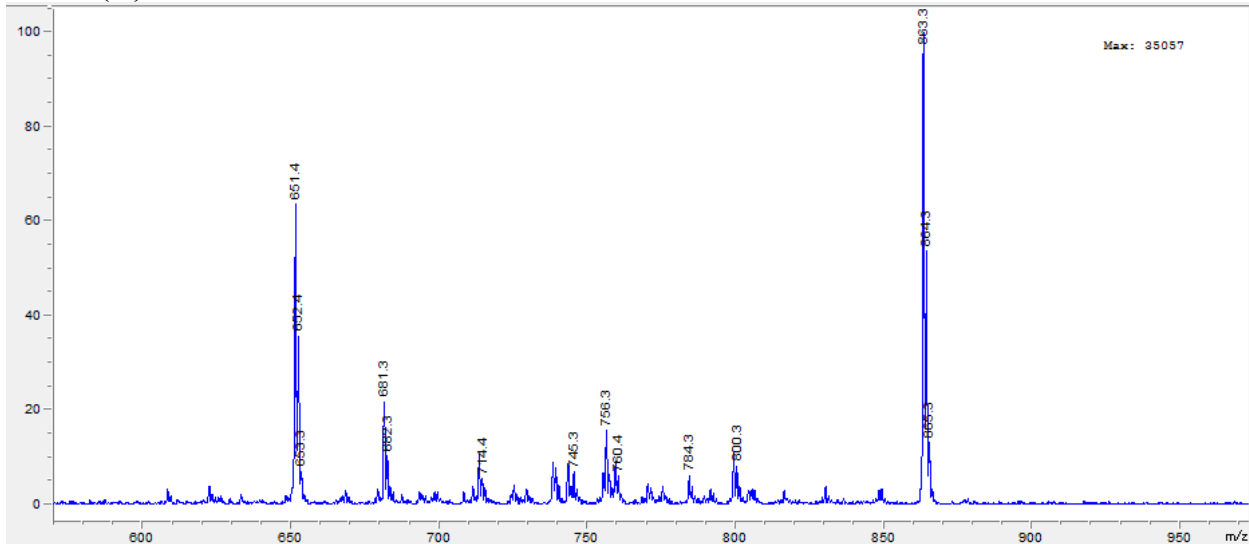
No reaction observed. The peak at 681.4 corresponds to a presumed methoxide addition product (shown above) [M+H]⁺. 713.4 corresponds to a different methanol adduct [M+H+MeOH]⁺.

Silver(I)



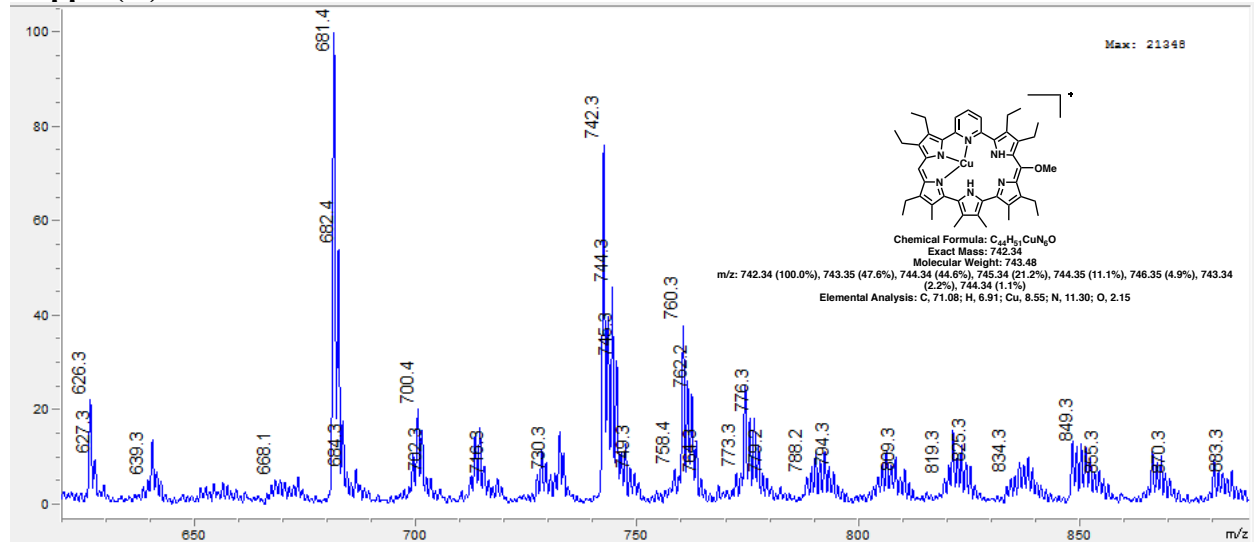
The peak at 787.3 corresponds to a putative silver(I) complex. A proposed structure is shown as an inset.

Cobalt(II)



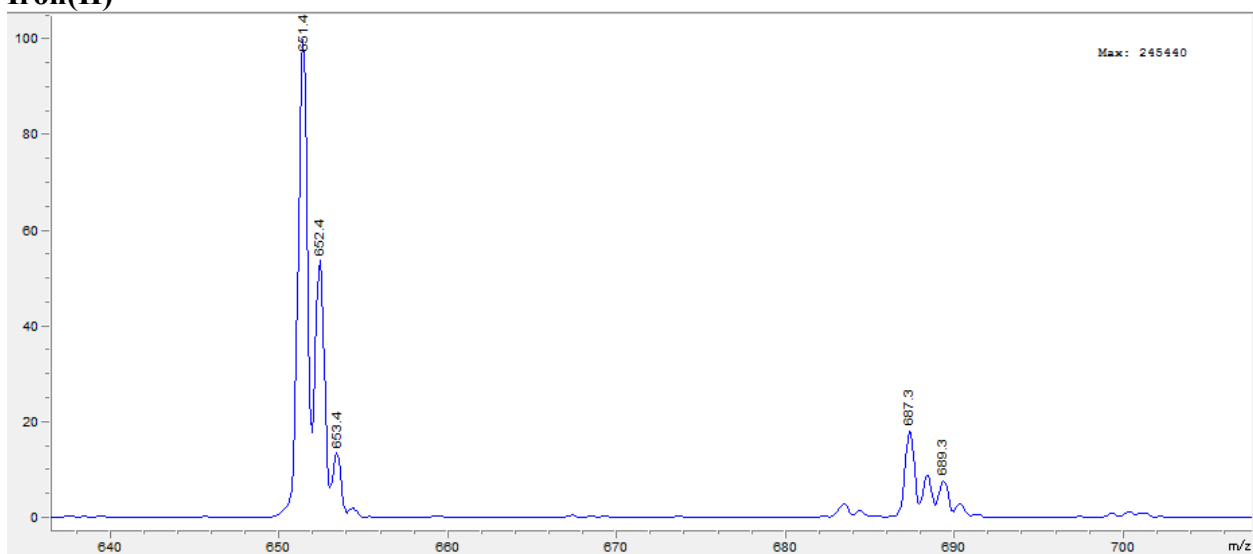
No evidence of metalation observed.

Copper(II)



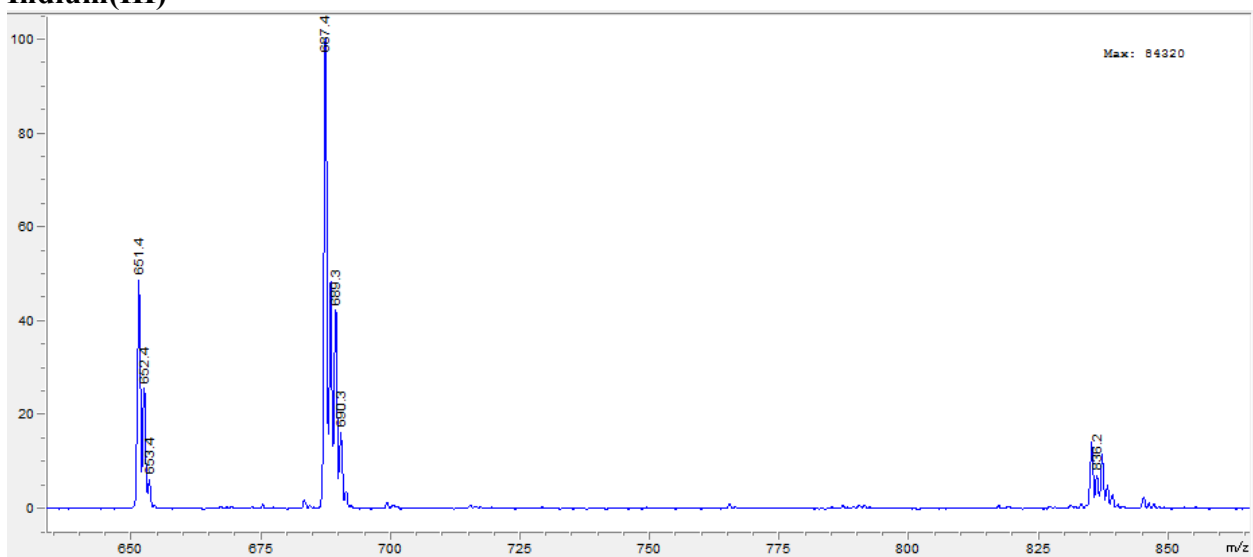
The peak at 742.3 is consistent with formation of a copper(II) complex of the methoxide addition product. A proposed structure is shown as an inset.

Iron(II)



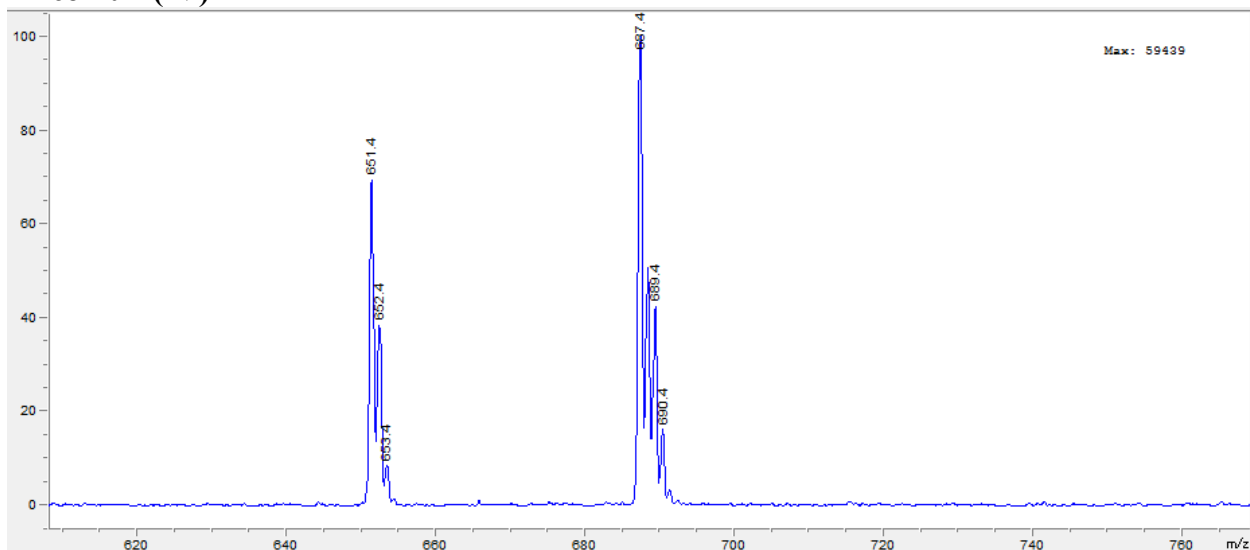
No evidence of metalation is observed.

Indium(III)



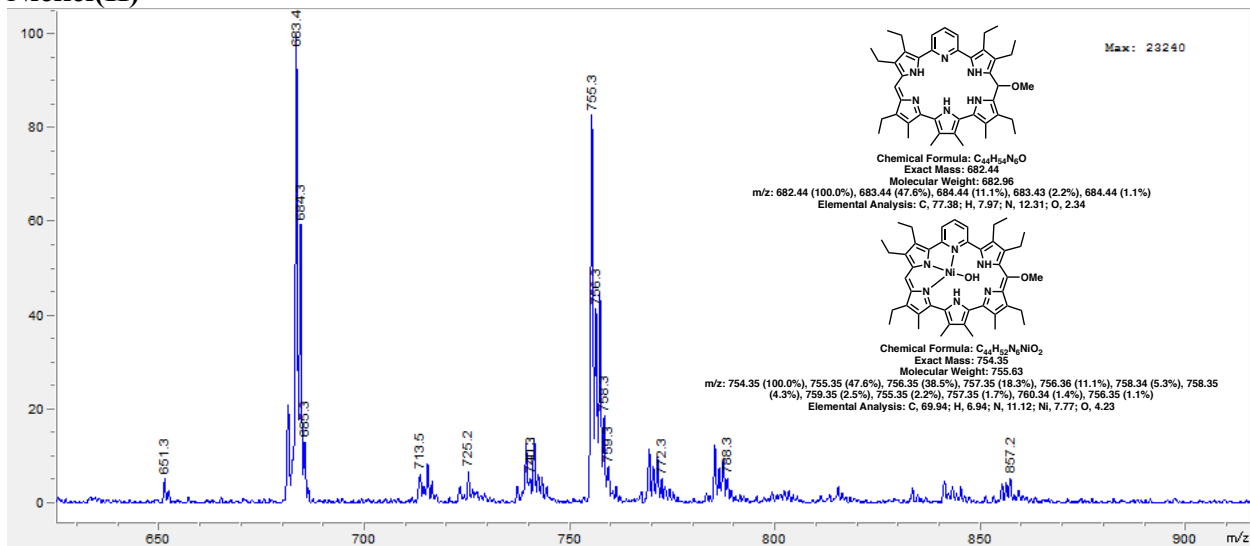
No evidence of metalation is observed.

Zirconium(IV)



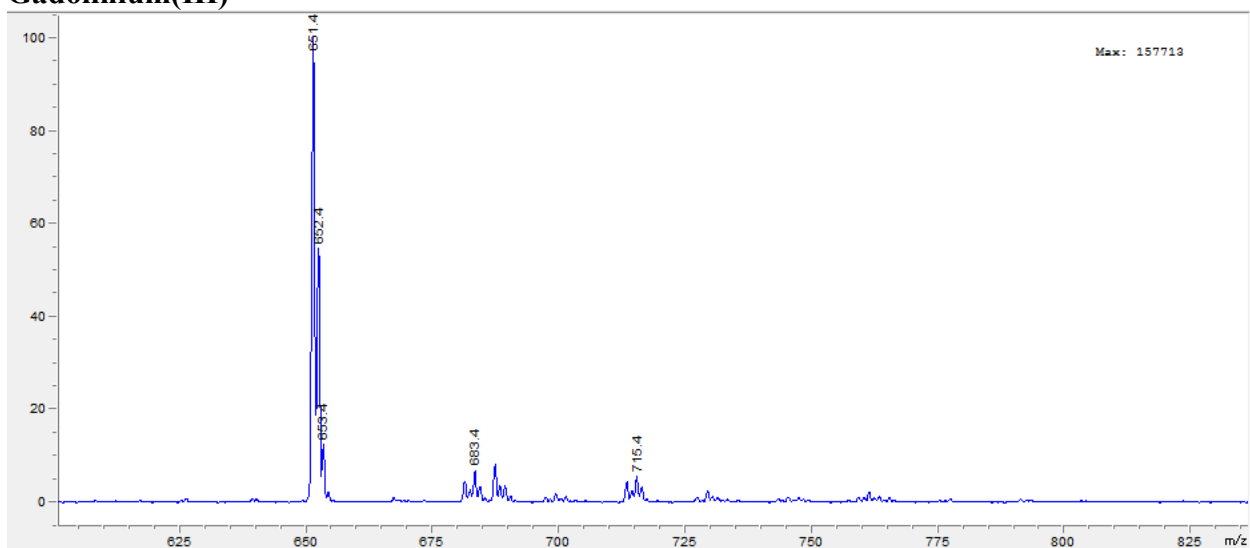
No evidence of metalation is observed.

Nickel(II)



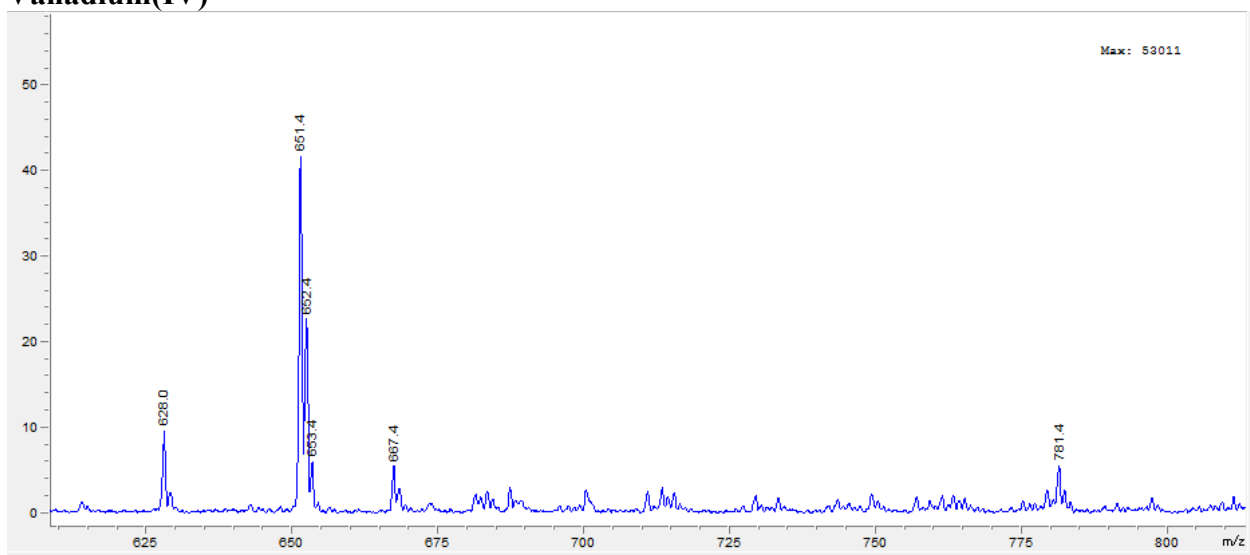
The peak seen at 683.4 amu corresponds to the reduced form of the methoxide addition product. The peak at 755.3 amu corresponds to a putative nickel complex. Proposed structures are shown as insets.

Gadolinium(III)



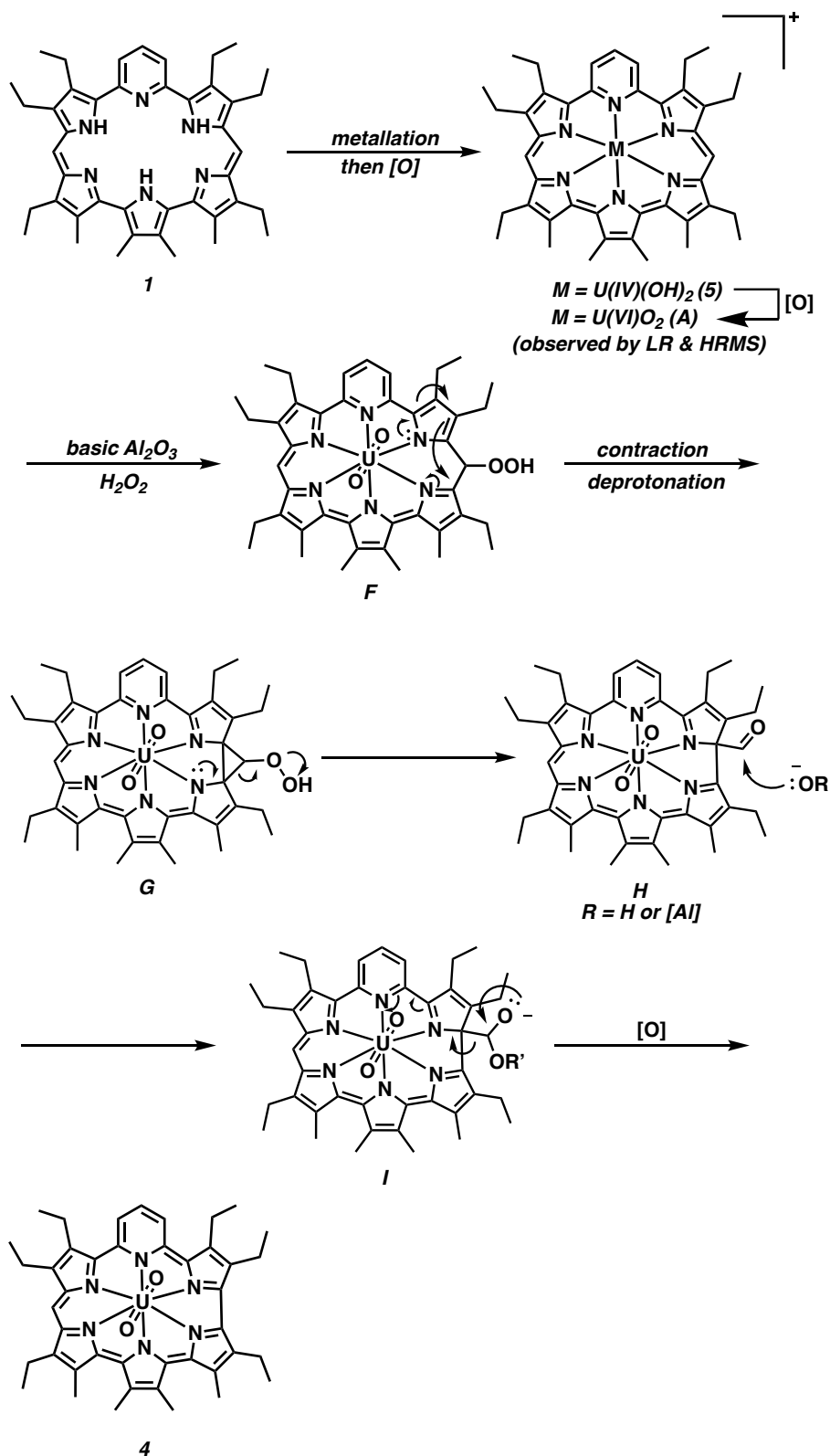
No evidence of metalation is observed.

Vanadium(IV)



No evidence of metalation is observed.

Alternative Mechanism



Scheme S1. An alternative mechanism to facilitate the ring contraction yielding uranyl complex **4**.

Density Functional Theory (DFT) Calculations.

Theoretical calculations were performed with the Gaussian16 program suite using the Texas Advanced Computing Center's (TACC) Stampede2 supercomputer. Calculations were carried out using the density functional theory (DFT) method with Becke's three-parameter hybrid exchange functionals and the Lee-Yang-Parr correlation functional (B3LYP) employing the 6-31G+(d) basis set for the C, H, N, O atoms. The uranyl atom was treated with a Stuttgart-Dresden (ECP) pseudopotential in combination with the appropriate basis set, which will be denoted as B1. Geometry optimizations were carried out based on the crystal structure metric parameters. The nature of the extrema were verified with analytical frequency calculations. To simulate the steady-state absorption spectra, time-dependent (TD) DFT calculations were carried out at the B3LYP/6-31G(d) or B1 level. Anisotropy of the current-induced density (ACID) plots were obtained by employing a continuous set of gauge transformations (CSGT) to calculate the current densities, and the results were plotted using POV-Ray 3.7 on a Linux system.

Optimized Structures of Ligand and Uranyl Complex

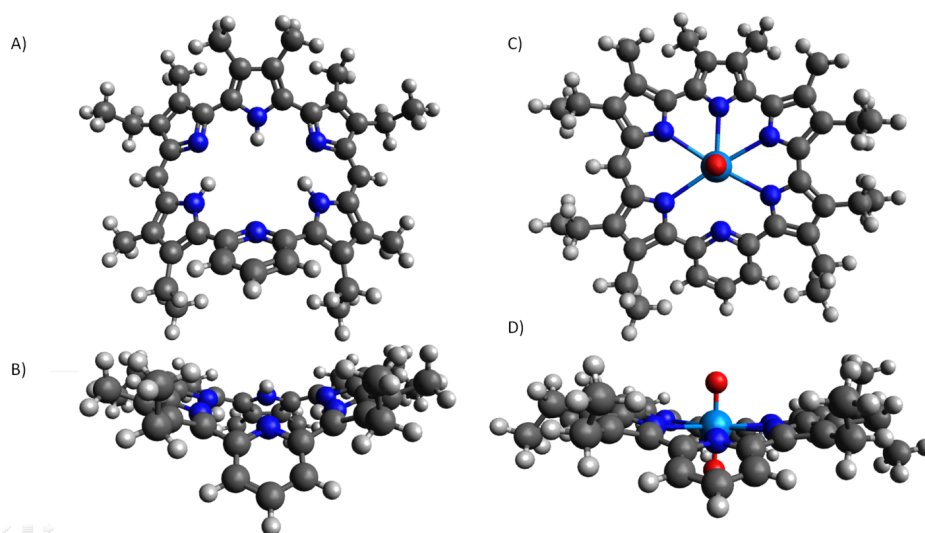
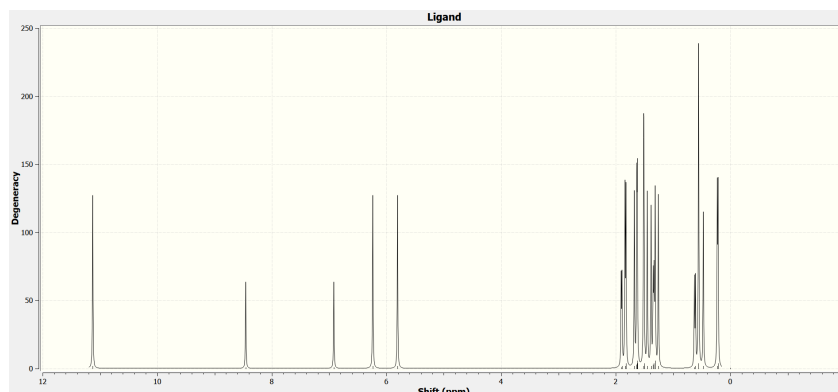


Figure S1: Ligand (1) viewed from the (a) top and (b) side. Also shown is the uranyl complex (4) in (c) top and (d) side views

Predicted ¹H NMR Spectra of Ligand 1 and Uranyl Complex 4.



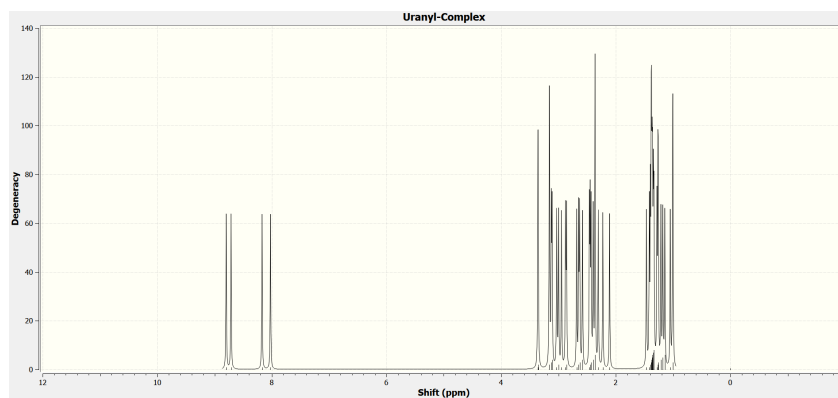


Figure S2: Predicted ^1H NMR spectra of (top) **1** and (bottom) **4**.

ACID Plot of Pyrihexaphyrin **1**

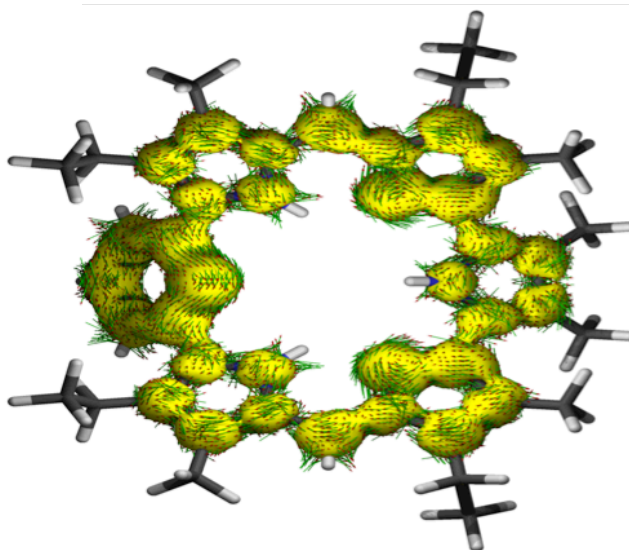


Figure S3: ACID map (standard isovalue of 0.05) of pyrihexaphyrin **1**.

Electrostatic Potential Map of Pyrihexaphyrin (1)

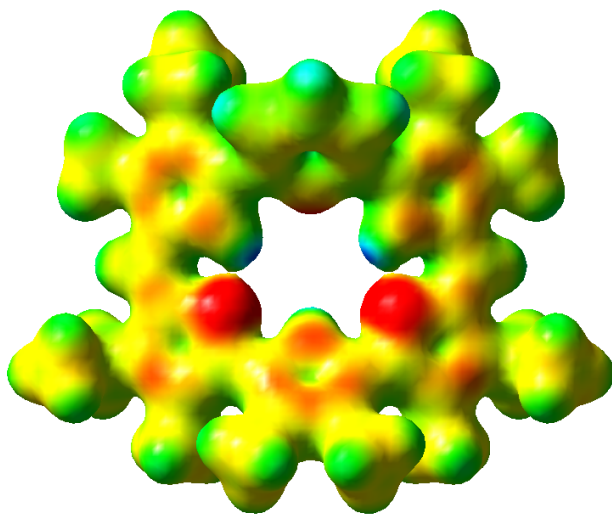


Figure S4: Electrostatic potential (ESP) of ligand **1** mapped on the electron density surface at an isosurface value of 0.02 au. Potential ranges were consistent at -0.02 au to 0.25 au. Red indicates a negative ESP (high electron density), green indicates neutral, and blue indicates positive ESP (low electron density).

ACID Plot of Contracted Pyrihexaphyrin-Uranyl Complex 4

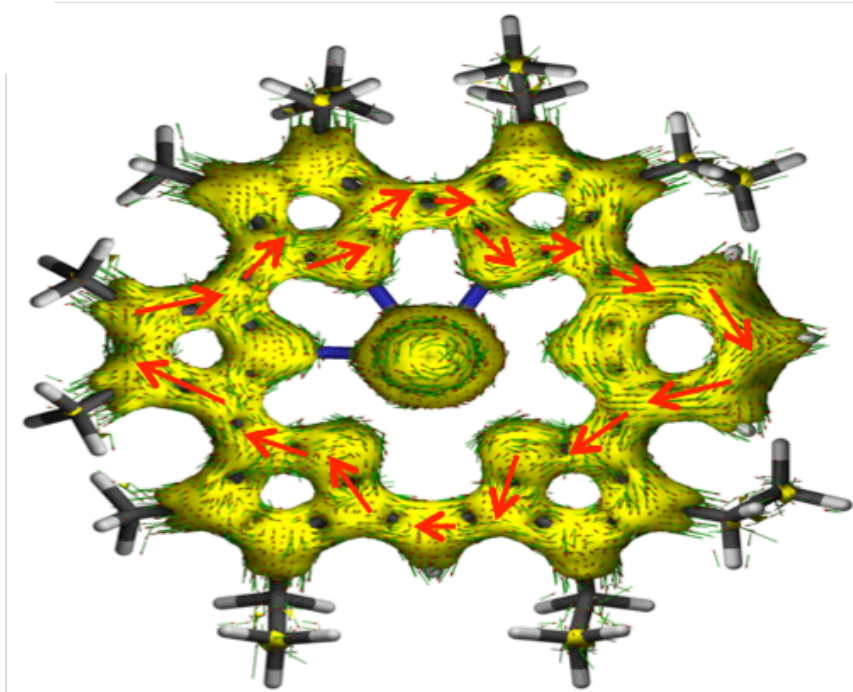
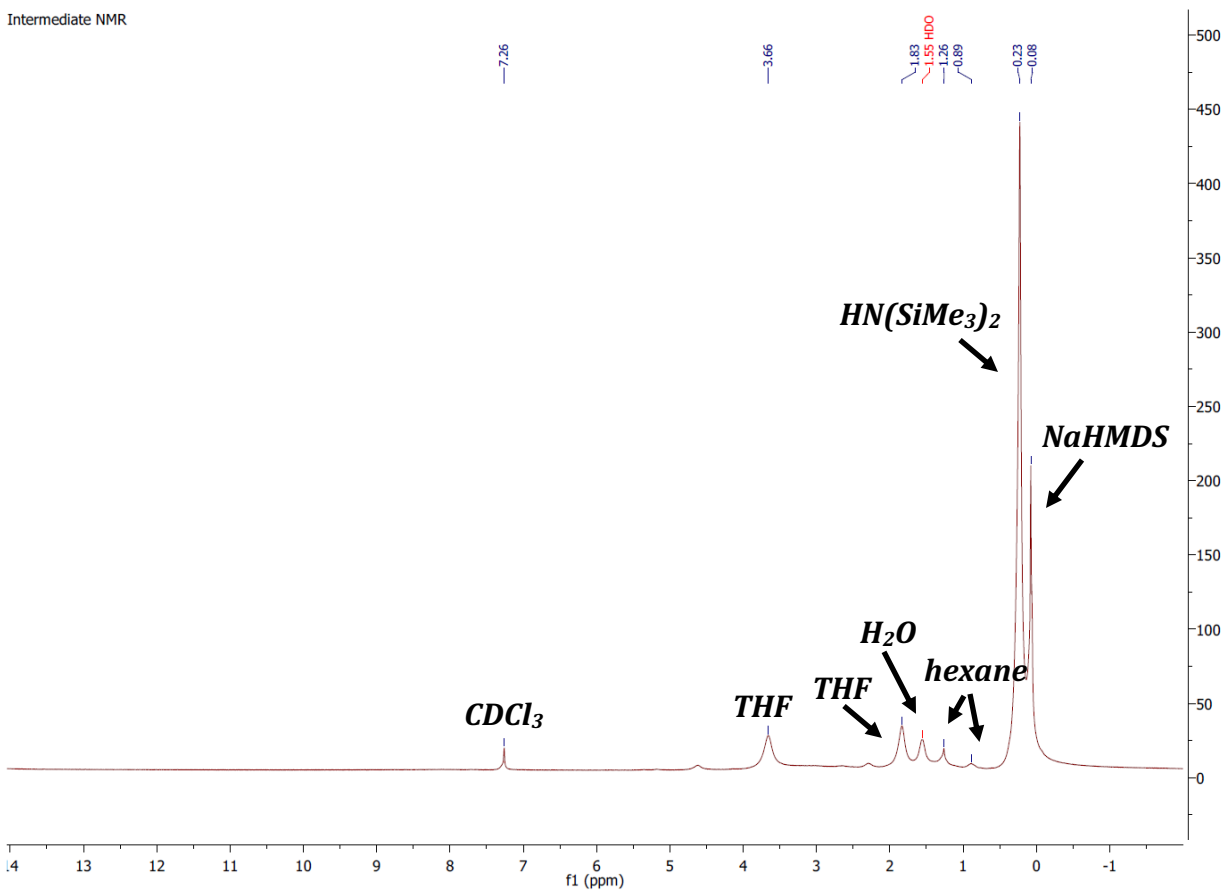


Figure S5: ACID map (standard isovalue of 0.05) of contracted pyrihexaphyrin-uranyl complex **4**.

NMR of Intermediate 5 Under Anaerobic Conditions



LR & HRMS Spectra

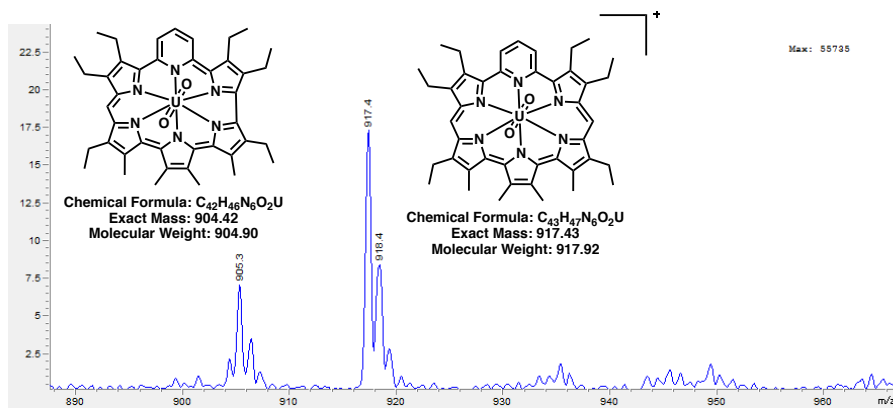


Figure S7: Low-resolution mass spectrum showing ring-contracted contracted pyrihexaphyrin **4** ($[\text{M}+\text{H}^+]$ at 905) and cationic intermediate **A** ($[\text{M}^+]$ at 917). Proposed structures are shown as inserts.

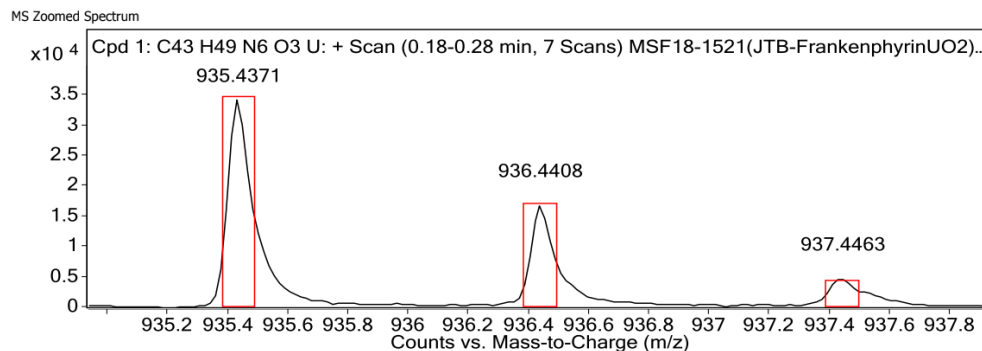


Figure S8: HRMS (ESI⁺) calcd. for C₄₃H₄₇N₆O₂U + H₂O as [M⁺] 935.4368, found 935.4368.

Electrostatic Potential Map and ACID Plot of Intermediate *A*.

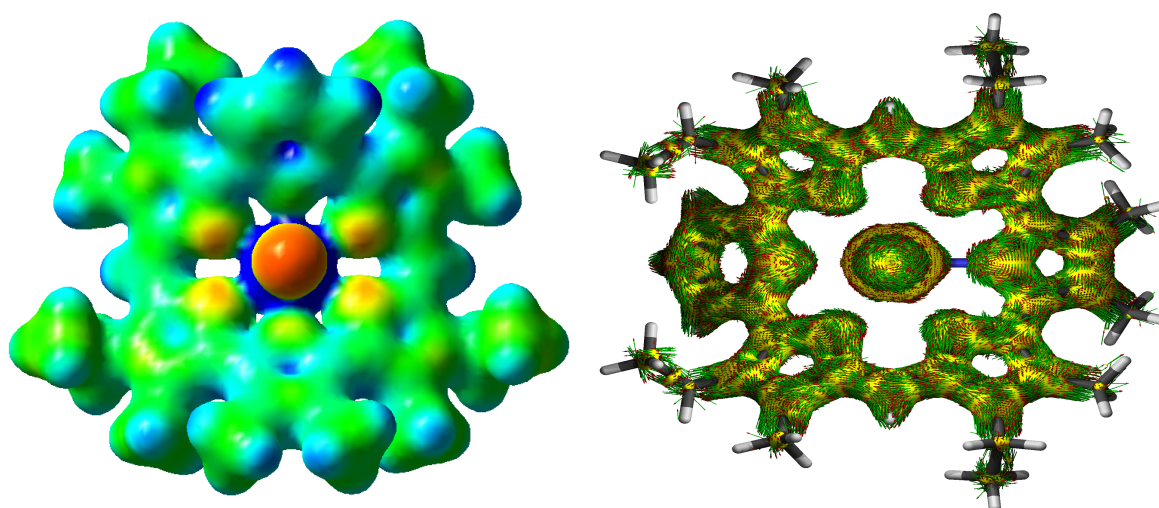


Figure S9: (Left) Electrostatic potential (ESP) of intermediate *A* mapped on the electron density surface at an isosurface value of 0.02 au. Potential ranges were consistent at -0.02 au to 0.25 au- the same values as those used for pyrihexaphyrin **1**. Red indicates a negative ESP (high electron density), green indicates neutral, and blue indicates positive ESP (low electron density). (Right) ACID map (standard isovalue of 0.05) of cationic intermediate *A*.

Calculated Molecular Orbitals for Ligand **1** and Uranyl Complex **4**

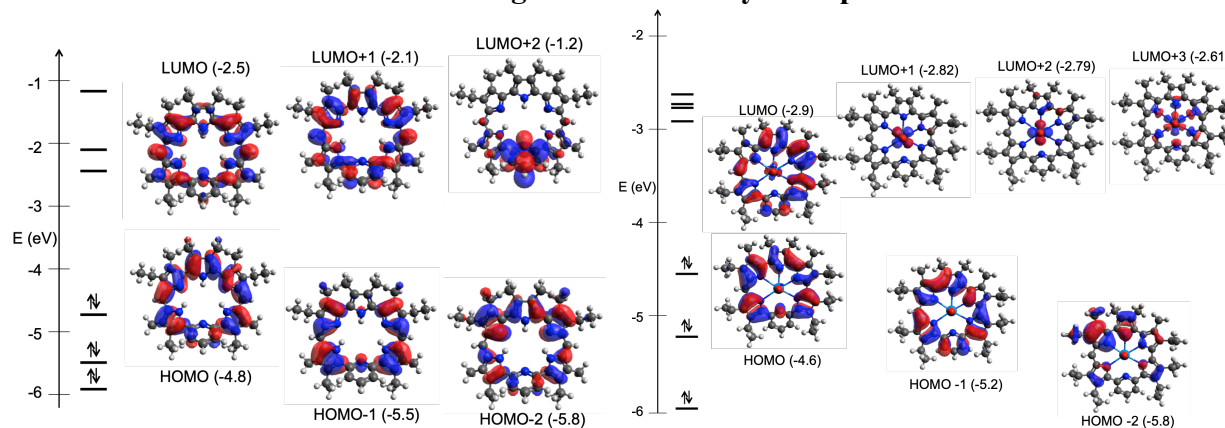


Figure S10: Calculated molecular orbitals for (left) ligand **1** and (right) uranyl complex **4**.

X-Ray Crystallographic Data

X-ray experimental for C₄₃H₅₀N₆ (pyrihexaphyrin **1**): Crystals grew as clusters of very dark prisms by slow evaporation of a 1:1 solution of dichloromethane: hexanes. The data crystal was cut from a larger crystal and had approximate dimensions: 0.28 x 0.20 x 0.13 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ -focus Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$) with collimating mirror monochromators. A total of 1218 frames of data were collected using ω -scans with a scan range of 1° and a counting time of 9 seconds per frame using a detector offset of $\pm 41.6^\circ$ and a counting time of 34 seconds per frame using a detector offset of $\pm 112^\circ$. The data were collected at 100 K using an Oxford Cryostream low temperature device. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.39.46f.¹ The structure was solved by direct methods using SHELXT² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.³ Structure analysis was aided by use of the programs PLATON⁴ and WinGX.⁵ The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atoms bound to the nitrogen atoms of the macrocycle, N2, N4 and N6, were observed in a ΔF map and refined with isotropic displacement parameters.

Three of the ethyl groups were disordered. The disorder involved the orientation of the methyl group to be on opposite sides of the mean plane through the macrocycle. The disorder was modeled in the same manner for all three groups, which had different degrees of disorder. For example, for one group, the variable x was assigned to the site occupancy factors for the carbon atoms of one component. The variable $(1-x)$ was assigned to the site occupancy factors for the carbon atoms of the alternate component. A common isotropic displacement parameter was refined for all four carbon atoms while refining x . Hydrogen atoms were added in idealized positions. Upon convergence for x , the site occupancy factors were fixed and individual atom displacement parameters were refined. The geometry of the two groups were restrained to be equivalent throughout the refinement process.

A molecule of what appeared to be diethyl ether was found to be badly disordered along a column near $1/4, 3/4, z$. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to this solvent molecule were removed by use of the utility SQUEEZE⁶ in PLATON. PLATON was used as incorporated in WinGX.

The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0746 \cdot P)^2 + (11.6296 \cdot P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.165, with $R(F)$ equal to 0.0613 and a goodness of fit, S , = 1.07. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁷ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁸ All figures were generated using SHELXTL/PC.⁹ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found below.

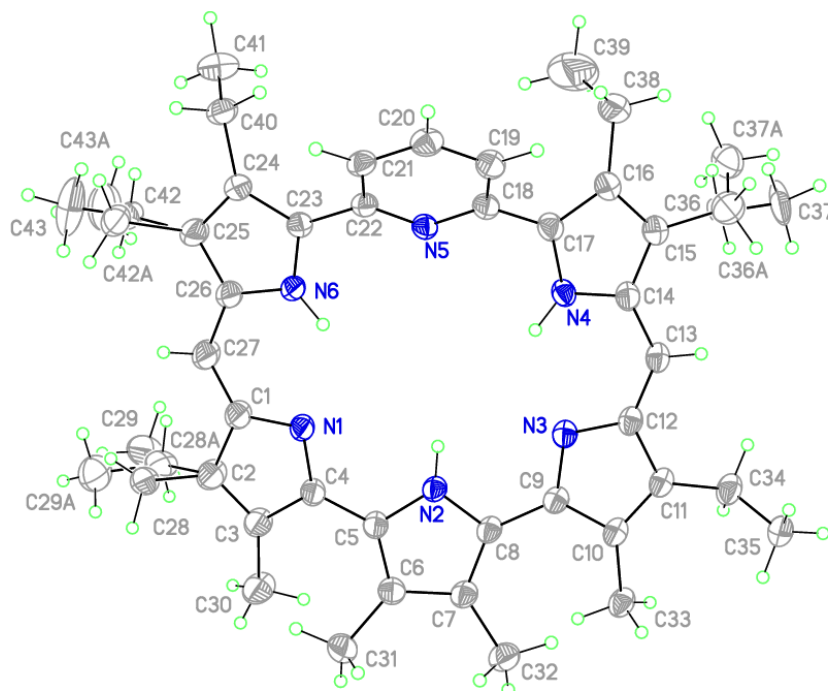


Figure S11. View of **1** showing the atom-labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The lower occupancy carbon atoms of the disordered ethyl groups have labels append by an A.

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	C ₄₃ H ₅₀ N ₆	
Formula weight	650.89	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	I 2/a	
Unit cell dimensions	a = 25.0636(6) Å	α = 90°.
	b = 15.3118(3) Å	β = 100.921(2)°.
	c = 21.2557(5) Å	γ = 90°.
Volume	8009.5(3) Å ³	
Z	8	
Density (calculated)	1.080 Mg/m ³	
Absorption coefficient	0.493 mm ⁻¹	
F(000)	2800	
Crystal size	0.28 x 0.20 x 0.13 mm ³	
Theta range for data collection	3.400 to 75.782°.	
Index ranges	-31 ≤ h ≤ 30, -19 ≤ k ≤ 18, -25 ≤ l ≤ 26	

Reflections collected	27722
Independent reflections	8203 [R(int) = 0.0230]
Completeness to theta = 67.684°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00 and 0.929
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8203 / 423 / 521
Goodness-of-fit on F ²	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0613, wR2 = 0.1617
R indices (all data)	R1 = 0.0644, wR2 = 0.1646
Extinction coefficient	n/a
Largest diff. peak and hole	0.308 and -0.291 e.Å ⁻³
CCDC number	1893882

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C1	6189(1)	9173(1)	5294(1)	39(1)
C2	5917(1)	9713(1)	5702(1)	50(1)
C3	5746(1)	9162(1)	6124(1)	42(1)
C4	5932(1)	8298(1)	5978(1)	30(1)
C5	5863(1)	7490(1)	6311(1)	28(1)
C6	5887(1)	7282(1)	6955(1)	30(1)
C7	5774(1)	6378(1)	6991(1)	29(1)
C8	5687(1)	6049(1)	6367(1)	26(1)
C9	5542(1)	5207(1)	6071(1)	26(1)
C10	5160(1)	4565(1)	6240(1)	28(1)
C11	5114(1)	3935(1)	5781(1)	29(1)
C12	5468(1)	4198(1)	5345(1)	27(1)
C13	5554(1)	3771(1)	4809(1)	29(1)
C14	5912(1)	4018(1)	4396(1)	29(1)
C15	6037(1)	3576(1)	3867(1)	38(1)
C16	6460(1)	4039(1)	3661(1)	38(1)
C17	6581(1)	4760(1)	4067(1)	29(1)

C18	7012(1)	5417(1)	4082(1)	27(1)
C19	7540(1)	5136(1)	4060(1)	31(1)
C20	7945(1)	5744(1)	4067(1)	31(1)
C21	7818(1)	6619(1)	4089(1)	27(1)
C22	7280(1)	6856(1)	4103(1)	24(1)
C23	7133(1)	7783(1)	4114(1)	25(1)
C24	7308(1)	8501(1)	3797(1)	31(1)
C25	7058(1)	9244(1)	4005(1)	42(1)
C26	6740(1)	8962(1)	4443(1)	36(1)
C27	6447(1)	9463(1)	4823(1)	46(1)
C28	5881(2)	10691(2)	5681(2)	43(1)
C29	5427(2)	10993(2)	5134(2)	62(1)
C28A	5608(5)	10634(7)	5381(6)	43(2)
C29A	6030(4)	11305(4)	5636(6)	56(2)
C30	5378(1)	9373(1)	6585(1)	55(1)
C31	6061(1)	7868(1)	7525(1)	39(1)
C32	5794(1)	5877(1)	7602(1)	37(1)
C33	4843(1)	4630(1)	6766(1)	33(1)
C34	4762(1)	3134(1)	5730(1)	37(1)
C35	4946(1)	2471(1)	6264(1)	47(1)
C36	5702(3)	2809(4)	3546(4)	37(1)
C37	6013(2)	1972(2)	3732(3)	59(1)
C36A	5882(3)	2658(6)	3632(4)	46(2)
C37A	5562(2)	2684(3)	2953(2)	49(1)
C38	6704(1)	3827(2)	3088(1)	61(1)
C39	6515(2)	4391(3)	2528(2)	117(2)
C40	7668(1)	8492(1)	3303(1)	35(1)
C41	7378(1)	8723(2)	2630(1)	50(1)
C42	7034(2)	10165(3)	3739(2)	34(1)
C43	7583(2)	10585(3)	3964(3)	79(2)
C42A	7264(2)	10190(4)	3931(3)	40(1)
C43A	6823(2)	10660(3)	3471(3)	67(2)
N1	6181(1)	8300(1)	5480(1)	29(1)
N2	5760(1)	6729(1)	5969(1)	26(1)
N3	5722(1)	4990(1)	5546(1)	26(1)
N4	6244(1)	4743(1)	4497(1)	26(1)

N5	6882(1)	6266(1)	4115(1)	25(1)
N6	6787(1)	8072(1)	4488(1)	27(1)

Table 3. Bond lengths [Å] and angles [°] for **1**.

C1-C27	1.366(3)	C14-C15	1.396(3)
C1-N1	1.396(2)	C15-C16	1.413(3)
C1-C2	1.458(3)	C15-C36A	1.518(10)
C2-C3	1.359(3)	C15-C36	1.527(7)
C2-C28	1.501(3)	C16-C17	1.398(2)
C2-C28A	1.690(13)	C16-C38	1.500(3)
C3-C4	1.457(2)	C17-N4	1.360(2)
C3-C30	1.501(3)	C17-C18	1.471(2)
C4-N1	1.326(2)	C18-N5	1.345(2)
C4-C5	1.453(2)	C18-C19	1.401(2)
C5-N2	1.371(2)	C19-C20	1.376(3)
C5-C6	1.396(2)	C19-H19	0.95
C6-C7	1.418(2)	C20-C21	1.381(2)
C6-C31	1.503(3)	C20-H20	0.95
C7-C8	1.396(2)	C21-C22	1.402(2)
C7-C32	1.501(2)	C21-H21	0.95
C8-N2	1.375(2)	C22-N5	1.348(2)
C8-C9	1.451(2)	C22-C23	1.468(2)
C9-N3	1.324(2)	C23-N6	1.357(2)
C9-C10	1.463(2)	C23-C24	1.403(2)
C10-C11	1.361(3)	C24-C25	1.409(3)
C10-C33	1.495(2)	C24-C40	1.508(2)
C11-C12	1.455(2)	C25-C26	1.405(3)
C11-C34	1.503(2)	C25-C42	1.516(5)
C12-C13	1.366(2)	C25-C42A	1.555(6)
C12-N3	1.398(2)	C26-N6	1.371(2)
C13-C14	1.421(2)	C26-C27	1.415(3)
C13-H13	0.95	C27-H27	0.95
C14-N4	1.379(2)	C28-C29	1.537(4)

C28-H28A	0.99	C37-H37F	0.98
C28-H28B	0.99	C36A-C37A	1.514(7)
C29-H29A	0.98	C36A-H36A	0.99
C29-H29B	0.98	C36A-H36B	0.99
C29-H29C	0.98	C37A-H37A	0.98
C28A-C29A	1.501(9)	C37A-H37B	0.98
C28A-H28C	0.99	C37A-H37C	0.98
C28A-H28D	0.99	C38-C39	1.473(5)
C29A-H29D	0.98	C38-H38A	0.99
C29A-H29E	0.98	C38-H38B	0.99
C29A-H29F	0.98	C39-H39A	0.98
C30-H30A	0.98	C39-H39B	0.98
C30-H30B	0.98	C39-H39C	0.98
C30-H30C	0.98	C40-C41	1.518(3)
C31-H31A	0.98	C40-H40A	0.99
C31-H31B	0.98	C40-H40B	0.99
C31-H31C	0.98	C41-H41A	0.98
C32-H32A	0.98	C41-H41B	0.98
C32-H32B	0.98	C41-H41C	0.98
C32-H32C	0.98	C42-C43	1.514(6)
C33-H33A	0.98	C42-H42A	0.99
C33-H33B	0.98	C42-H42B	0.99
C33-H33C	0.98	C43-H43A	0.98
C34-C35	1.527(3)	C43-H43B	0.98
C34-H34A	0.99	C43-H43C	0.98
C34-H34B	0.99	C42A-C43A	1.511(6)
C35-H35A	0.98	C42A-H42C	0.99
C35-H35B	0.98	C42A-H42D	0.99
C35-H35C	0.98	C43A-H43D	0.98
C36-C37	1.514(6)	C43A-H43E	0.98
C36-H36C	0.99	C43A-H43F	0.98
C36-H36D	0.99	N2-H2N	0.92(2)
C37-H37D	0.98	N4-H4N	0.91(2)
C37-H37E	0.98	N6-H6N	0.91(2)
C27-C1-N1	123.63(16)	C27-C1-C2	126.31(18)

N1-C1-C2	109.95(16)	C12-C13-C14	127.33(16)
C3-C2-C1	106.43(17)	C12-C13-H13	116.3
C3-C2-C28	127.90(19)	C14-C13-H13	116.3
C1-C2-C28	125.50(19)	N4-C14-C15	107.24(15)
C3-C2-C28A	127.4(4)	N4-C14-C13	123.35(16)
C1-C2-C28A	117.6(4)	C15-C14-C13	129.20(16)
C2-C3-C4	105.57(16)	C14-C15-C16	107.54(16)
C2-C3-C30	127.38(18)	C14-C15-C36A	129.2(4)
C4-C3-C30	126.59(17)	C16-C15-C36A	121.5(4)
N1-C4-C5	120.63(15)	C14-C15-C36	123.1(3)
N1-C4-C3	112.74(15)	C16-C15-C36	128.9(3)
C5-C4-C3	126.63(15)	C17-C16-C15	107.09(16)
N2-C5-C6	107.20(15)	C17-C16-C38	126.71(18)
N2-C5-C4	119.49(15)	C15-C16-C38	126.07(18)
C6-C5-C4	133.31(16)	N4-C17-C16	108.01(15)
C5-C6-C7	107.59(15)	N4-C17-C18	123.09(15)
C5-C6-C31	127.28(16)	C16-C17-C18	128.79(16)
C7-C6-C31	124.80(17)	N5-C18-C19	122.51(15)
C8-C7-C6	107.36(15)	N5-C18-C17	118.61(14)
C8-C7-C32	127.68(16)	C19-C18-C17	118.89(15)
C6-C7-C32	124.78(16)	C20-C19-C18	119.51(16)
N2-C8-C7	107.20(15)	C20-C19-H19	120.2
N2-C8-C9	117.35(15)	C18-C19-H19	120.2
C7-C8-C9	135.45(15)	C19-C20-C21	118.79(15)
N3-C9-C8	119.38(14)	C19-C20-H20	120.6
N3-C9-C10	112.45(15)	C21-C20-H20	120.6
C8-C9-C10	127.82(15)	C20-C21-C22	118.80(15)
C11-C10-C9	105.70(15)	C20-C21-H21	120.6
C11-C10-C33	126.82(16)	C22-C21-H21	120.6
C9-C10-C33	127.22(16)	N5-C22-C21	122.97(15)
C10-C11-C12	106.33(15)	N5-C22-C23	117.35(14)
C10-C11-C34	126.76(16)	C21-C22-C23	119.67(15)
C12-C11-C34	126.91(16)	N6-C23-C24	108.64(15)
C13-C12-N3	122.33(15)	N6-C23-C22	120.94(14)
C13-C12-C11	127.58(16)	C24-C23-C22	130.40(15)
N3-C12-C11	110.09(15)	C23-C24-C25	106.46(15)

C23-C24-C40	127.61(16)	H29E-C29A-H29F	109.5
C25-C24-C40	125.86(16)	C3-C30-H30A	109.5
C26-C25-C24	107.64(16)	C3-C30-H30B	109.5
C26-C25-C42	122.9(2)	H30A-C30-H30B	109.5
C24-C25-C42	128.6(2)	C3-C30-H30C	109.5
C26-C25-C42A	126.4(3)	H30A-C30-H30C	109.5
C24-C25-C42A	123.0(3)	H30B-C30-H30C	109.5
N6-C26-C25	107.43(16)	C6-C31-H31A	109.5
N6-C26-C27	123.10(17)	C6-C31-H31B	109.5
C25-C26-C27	129.30(17)	H31A-C31-H31B	109.5
C1-C27-C26	127.66(18)	C6-C31-H31C	109.5
C1-C27-H27	116.2	H31A-C31-H31C	109.5
C26-C27-H27	116.2	H31B-C31-H31C	109.5
C2-C28-C29	110.8(3)	C7-C32-H32A	109.5
C2-C28-H28A	109.5	C7-C32-H32B	109.5
C29-C28-H28A	109.5	H32A-C32-H32B	109.5
C2-C28-H28B	109.5	C7-C32-H32C	109.5
C29-C28-H28B	109.5	H32A-C32-H32C	109.5
H28A-C28-H28B	108.1	H32B-C32-H32C	109.5
C28-C29-H29A	109.5	C10-C33-H33A	109.5
C28-C29-H29B	109.5	C10-C33-H33B	109.5
H29A-C29-H29B	109.5	H33A-C33-H33B	109.5
C28-C29-H29C	109.5	C10-C33-H33C	109.5
H29A-C29-H29C	109.5	H33A-C33-H33C	109.5
H29B-C29-H29C	109.5	H33B-C33-H33C	109.5
C29A-C28A-C2	100.8(8)	C11-C34-C35	113.47(17)
C29A-C28A-H28C	111.6	C11-C34-H34A	108.9
C2-C28A-H28C	111.6	C35-C34-H34A	108.9
C29A-C28A-H28D	111.6	C11-C34-H34B	108.9
C2-C28A-H28D	111.6	C35-C34-H34B	108.9
H28C-C28A-H28D	109.4	H34A-C34-H34B	107.7
C28A-C29A-H29D	109.5	C34-C35-H35A	109.5
C28A-C29A-H29E	109.5	C34-C35-H35B	109.5
H29D-C29A-H29E	109.5	H35A-C35-H35B	109.5
C28A-C29A-H29F	109.5	C34-C35-H35C	109.5
H29D-C29A-H29F	109.5	H35A-C35-H35C	109.5

H35B-C35-H35C	109.5	H39B-C39-H39C	109.5
C37-C36-C15	108.8(4)	C24-C40-C41	114.25(16)
C37-C36-H36C	109.9	C24-C40-H40A	108.7
C15-C36-H36C	109.9	C41-C40-H40A	108.7
C37-C36-H36D	109.9	C24-C40-H40B	108.7
C15-C36-H36D	109.9	C41-C40-H40B	108.7
H36C-C36-H36D	108.3	H40A-C40-H40B	107.6
C36-C37-H37D	109.5	C40-C41-H41A	109.5
C36-C37-H37E	109.5	C40-C41-H41B	109.5
H37D-C37-H37E	109.5	H41A-C41-H41B	109.5
C36-C37-H37F	109.5	C40-C41-H41C	109.5
H37D-C37-H37F	109.5	H41A-C41-H41C	109.5
H37E-C37-H37F	109.5	H41B-C41-H41C	109.5
C37A-C36A-C15	110.2(6)	C43-C42-C25	107.9(4)
C37A-C36A-H36A	109.6	C43-C42-H42A	110.1
C15-C36A-H36A	109.6	C25-C42-H42A	110.1
C37A-C36A-H36B	109.6	C43-C42-H42B	110.1
C15-C36A-H36B	109.6	C25-C42-H42B	110.1
H36A-C36A-H36B	108.1	H42A-C42-H42B	108.4
C36A-C37A-H37A	109.5	C42-C43-H43A	109.5
C36A-C37A-H37B	109.5	C42-C43-H43B	109.5
H37A-C37A-H37B	109.5	H43A-C43-H43B	109.5
C36A-C37A-H37C	109.5	C42-C43-H43C	109.5
H37A-C37A-H37C	109.5	H43A-C43-H43C	109.5
H37B-C37A-H37C	109.5	H43B-C43-H43C	109.5
C39-C38-C16	114.2(3)	C43A-C42A-C25	107.1(4)
C39-C38-H38A	108.7	C43A-C42A-H42C	110.3
C16-C38-H38A	108.7	C25-C42A-H42C	110.3
C39-C38-H38B	108.7	C43A-C42A-H42D	110.3
C16-C38-H38B	108.7	C25-C42A-H42D	110.3
H38A-C38-H38B	107.6	H42C-C42A-H42D	108.5
C38-C39-H39A	109.5	C42A-C43A-H43D	109.5
C38-C39-H39B	109.5	C42A-C43A-H43E	109.5
H39A-C39-H39B	109.5	H43D-C43A-H43E	109.5
C38-C39-H39C	109.5	C42A-C43A-H43F	109.5
H39A-C39-H39C	109.5	H43D-C43A-H43F	109.5

H43E-C43A-H43F	109.5	C17-N4-H4N	126.3(14)
C4-N1-C1	105.24(14)	C14-N4-H4N	123.6(14)
C5-N2-C8	110.55(14)	C18-N5-C22	117.36(14)
C5-N2-H2N	124.4(14)	C23-N6-C26	109.79(14)
C8-N2-H2N	124.6(14)	C23-N6-H6N	128.1(15)
C9-N3-C12	105.43(14)	C26-N6-H6N	121.7(15)
C17-N4-C14	110.09(14)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C1	52(1)	23(1)	50(1)	0(1)	29(1)	4(1)
C2	72(2)	26(1)	66(1)	2(1)	46(1)	9(1)
C3	55(1)	27(1)	55(1)	0(1)	35(1)	6(1)
C4	29(1)	24(1)	39(1)	-2(1)	15(1)	1(1)
C5	25(1)	24(1)	38(1)	-2(1)	15(1)	1(1)
C6	28(1)	28(1)	37(1)	-3(1)	15(1)	1(1)
C7	27(1)	29(1)	34(1)	1(1)	13(1)	1(1)
C8	22(1)	25(1)	35(1)	3(1)	13(1)	1(1)
C9	21(1)	26(1)	33(1)	4(1)	9(1)	3(1)
C10	23(1)	25(1)	37(1)	6(1)	9(1)	2(1)
C11	24(1)	26(1)	36(1)	6(1)	7(1)	1(1)
C12	22(1)	24(1)	36(1)	3(1)	6(1)	0(1)
C13	27(1)	24(1)	37(1)	1(1)	6(1)	-2(1)
C14	28(1)	23(1)	36(1)	-1(1)	7(1)	-1(1)
C15	47(1)	30(1)	39(1)	-6(1)	15(1)	-10(1)
C16	47(1)	29(1)	42(1)	-7(1)	19(1)	-7(1)
C17	27(1)	25(1)	35(1)	-2(1)	9(1)	2(1)
C18	26(1)	26(1)	30(1)	-2(1)	9(1)	2(1)
C19	29(1)	28(1)	39(1)	0(1)	13(1)	6(1)
C20	23(1)	36(1)	35(1)	2(1)	11(1)	6(1)
C21	24(1)	32(1)	28(1)	0(1)	9(1)	-2(1)

C22	24(1)	27(1)	23(1)	-1(1)	7(1)	0(1)
C23	25(1)	26(1)	26(1)	-1(1)	7(1)	-1(1)
C24	37(1)	29(1)	29(1)	1(1)	12(1)	-1(1)
C25	62(1)	27(1)	45(1)	4(1)	29(1)	3(1)
C26	49(1)	24(1)	40(1)	2(1)	22(1)	3(1)
C27	67(1)	23(1)	58(1)	3(1)	38(1)	6(1)
C28	66(2)	25(1)	45(2)	0(1)	27(2)	8(1)
C29	111(3)	31(1)	48(2)	9(1)	23(2)	28(2)
C28A	57(5)	33(4)	44(4)	0(4)	24(4)	16(4)
C29A	63(6)	41(5)	66(6)	3(4)	23(5)	5(5)
C30	73(2)	34(1)	72(2)	4(1)	51(1)	13(1)
C31	46(1)	35(1)	42(1)	-7(1)	19(1)	-3(1)
C32	41(1)	37(1)	36(1)	3(1)	15(1)	0(1)
C33	31(1)	30(1)	44(1)	6(1)	17(1)	1(1)
C34	36(1)	31(1)	45(1)	4(1)	12(1)	-8(1)
C35	71(2)	27(1)	49(1)	3(1)	27(1)	-2(1)
C36	39(3)	27(3)	50(3)	-19(2)	21(2)	-13(2)
C37	54(2)	16(2)	118(4)	-13(2)	41(3)	-5(2)
C36A	41(4)	46(4)	54(3)	-3(3)	17(3)	-7(3)
C37A	44(2)	45(2)	59(3)	-11(2)	16(2)	-10(2)
C38	87(2)	50(1)	57(1)	-22(1)	42(1)	-28(1)
C39	215(5)	96(3)	51(2)	5(2)	54(3)	11(3)
C40	39(1)	35(1)	34(1)	3(1)	16(1)	2(1)
C41	51(1)	67(2)	35(1)	4(1)	18(1)	7(1)
C42	39(3)	27(2)	40(2)	7(2)	17(2)	5(2)
C43	75(4)	45(3)	110(4)	23(3)	-5(3)	-26(3)
C42A	40(3)	34(2)	50(3)	3(2)	19(2)	-2(3)
C43A	76(4)	37(3)	83(4)	16(3)	3(3)	5(2)
N1	31(1)	22(1)	36(1)	-1(1)	15(1)	1(1)
N2	26(1)	23(1)	32(1)	1(1)	13(1)	0(1)
N3	21(1)	24(1)	34(1)	1(1)	8(1)	1(1)
N4	24(1)	22(1)	34(1)	-4(1)	9(1)	0(1)
N5	23(1)	24(1)	28(1)	-2(1)	8(1)	1(1)
N6	31(1)	23(1)	30(1)	1(1)	13(1)	0(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **1**.

	x	y	z	U(eq)
H13	5352	3249	4701	35
H19	7618	4531	4042	37
H20	8306	5564	4056	37
H21	8090	7053	4094	32
H27	6428	10073	4740	55
H28A	6233	10937	5618	52
H28B	5808	10911	6095	52
H29A	5487	10743	4729	93
H29B	5429	11632	5106	93
H29C	5075	10797	5218	93
H28C	5536	10615	4906	51
H28D	5263	10741	5531	51
H29D	5866	11888	5590	83
H29E	6327	11277	5396	83
H29F	6173	11189	6090	83
H30A	5598	9506	7007	82
H30B	5144	8871	6621	82
H30C	5154	9880	6429	82
H31A	6252	8377	7396	59
H31B	6305	7546	7861	59
H31C	5741	8061	7688	59
H32A	5456	5972	7761	55
H32B	6103	6078	7922	55
H32C	5835	5253	7520	55
H33A	4487	4352	6630	50
H33B	4792	5246	6865	50
H33C	5040	4333	7149	50
H34A	4762	2850	5311	44
H34B	4384	3313	5740	44
H35A	5317	2279	6251	70
H35B	4701	1966	6203	70

H35C	4939	2742	6679	70
H36C	5347	2787	3685	44
H36D	5634	2882	3075	44
H37D	6380	2025	3639	89
H37E	5824	1484	3487	89
H37F	6037	1864	4191	89
H36A	6215	2304	3647	55
H36B	5661	2380	3916	55
H37A	5270	3117	2923	73
H37B	5404	2108	2835	73
H37C	5803	2846	2659	73
H38A	7104	3876	3209	73
H38B	6617	3212	2963	73
H39A	6121	4325	2390	175
H39B	6697	4221	2178	175
H39C	6601	5001	2645	175
H40A	7830	7903	3295	42
H40B	7969	8911	3435	42
H41A	7073	8321	2498	75
H41B	7632	8674	2334	75
H41C	7241	9323	2625	75
H42A	6946	10150	3265	41
H42B	6748	10503	3895	41
H43A	7661	10612	4434	119
H43B	7581	11177	3789	119
H43C	7864	10238	3816	119
H42C	7334	10489	4352	48
H42D	7605	10179	3761	48
H43D	6827	10467	3033	100
H43E	6888	11291	3504	100
H43F	6469	10528	3580	100
H4N	6237(9)	5137(15)	4816(11)	38(6)
H6N	6631(10)	7759(16)	4772(12)	44(6)
H2N	5703(9)	6695(14)	5531(11)	33(5)

Table 6. Torsion angles [°] for **1**.

C27-C1-C2-C3	-176.6(3)	N2-C8-C9-C10	-141.16(17)
N1-C1-C2-C3	-0.4(3)	C7-C8-C9-C10	38.1(3)
C27-C1-C2-C28	-1.1(5)	N3-C9-C10-C11	-0.11(19)
N1-C1-C2-C28	175.2(3)	C8-C9-C10-C11	172.92(16)
C27-C1-C2-C28A	33.2(5)	N3-C9-C10-C33	-174.57(16)
N1-C1-C2-C28A	-150.6(4)	C8-C9-C10-C33	-1.5(3)
C1-C2-C3-C4	1.7(3)	C9-C10-C11-C12	0.23(18)
C28-C2-C3-C4	-173.7(3)	C33-C10-C11-C12	174.71(16)
C28A-C2-C3-C4	148.1(5)	C9-C10-C11-C34	-179.01(17)
C1-C2-C3-C30	-170.9(3)	C33-C10-C11-C34	-4.5(3)
C28-C2-C3-C30	13.8(5)	C10-C11-C12-C13	-179.81(17)
C28A-C2-C3-C30	-24.5(6)	C34-C11-C12-C13	-0.6(3)
C2-C3-C4-N1	-2.8(3)	C10-C11-C12-N3	-0.28(19)
C30-C3-C4-N1	169.9(2)	C34-C11-C12-N3	178.96(16)
C2-C3-C4-C5	178.0(2)	N3-C12-C13-C14	2.5(3)
C30-C3-C4-C5	-9.3(4)	C11-C12-C13-C14	-178.00(17)
N1-C4-C5-N2	-36.5(2)	C12-C13-C14-N4	1.8(3)
C3-C4-C5-N2	142.7(2)	C12-C13-C14-C15	175.8(2)
N1-C4-C5-C6	142.2(2)	N4-C14-C15-C16	1.5(2)
C3-C4-C5-C6	-38.7(3)	C13-C14-C15-C16	-173.35(19)
N2-C5-C6-C7	-2.26(19)	N4-C14-C15-C36A	166.2(4)
C4-C5-C6-C7	178.94(18)	C13-C14-C15-C36A	-8.6(5)
N2-C5-C6-C31	171.29(17)	N4-C14-C15-C36	-171.1(3)
C4-C5-C6-C31	-7.5(3)	C13-C14-C15-C36	14.0(4)
C5-C6-C7-C8	0.43(19)	C14-C15-C16-C17	-0.6(2)
C31-C6-C7-C8	-173.32(16)	C36A-C15-C16-C17	-166.8(4)
C5-C6-C7-C32	175.92(16)	C36-C15-C16-C17	171.4(4)
C31-C6-C7-C32	2.2(3)	C14-C15-C16-C38	-176.7(2)
C6-C7-C8-N2	1.56(18)	C36A-C15-C16-C38	17.1(5)
C32-C7-C8-N2	-173.76(16)	C36-C15-C16-C38	-4.7(5)
C6-C7-C8-C9	-177.77(18)	C15-C16-C17-N4	-0.5(2)
C32-C7-C8-C9	6.9(3)	C38-C16-C17-N4	175.6(2)
N2-C8-C9-N3	31.4(2)	C15-C16-C17-C18	175.90(18)
C7-C8-C9-N3	-149.28(19)	C38-C16-C17-C18	-8.1(4)

N4-C17-C18-N5	-50.8(2)	C3-C2-C28A-C29A	117.6(6)
C16-C17-C18-N5	133.3(2)	C1-C2-C28A-C29A	-99.3(7)
N4-C17-C18-C19	129.29(18)	C10-C11-C34-C35	-68.3(2)
C16-C17-C18-C19	-46.6(3)	C12-C11-C34-C35	112.7(2)
N5-C18-C19-C20	-0.7(3)	C14-C15-C36-C37	-105.1(4)
C17-C18-C19-C20	179.22(16)	C16-C15-C36-C37	84.0(6)
C18-C19-C20-C21	-0.5(3)	C14-C15-C36A-C37A	121.3(5)
C19-C20-C21-C22	-0.1(3)	C16-C15-C36A-C37A	-75.9(6)
C20-C21-C22-N5	2.0(2)	C17-C16-C38-C39	-73.1(4)
C20-C21-C22-C23	-178.86(15)	C15-C16-C38-C39	102.2(3)
N5-C22-C23-N6	39.6(2)	C23-C24-C40-C41	110.0(2)
C21-C22-C23-N6	-139.56(16)	C25-C24-C40-C41	-66.4(3)
N5-C22-C23-C24	-142.32(18)	C26-C25-C42-C43	116.2(4)
C21-C22-C23-C24	38.5(3)	C24-C25-C42-C43	-75.9(5)
N6-C23-C24-C25	1.0(2)	C26-C25-C42A-C43A	-87.2(5)
C22-C23-C24-C25	-177.22(18)	C24-C25-C42A-C43A	114.8(4)
N6-C23-C24-C40	-175.96(17)	C5-C4-N1-C1	-178.26(17)
C22-C23-C24-C40	5.8(3)	C3-C4-N1-C1	2.5(2)
C23-C24-C25-C26	0.1(2)	C27-C1-N1-C4	175.1(2)
C40-C24-C25-C26	177.16(19)	C2-C1-N1-C4	-1.3(2)
C23-C24-C25-C42	-169.3(3)	C6-C5-N2-C8	3.33(19)
C40-C24-C25-C42	7.7(4)	C4-C5-N2-C8	-177.68(14)
C23-C24-C25-C42A	161.7(3)	C7-C8-N2-C5	-3.06(18)
C40-C24-C25-C42A	-21.3(4)	C9-C8-N2-C5	176.41(14)
C24-C25-C26-N6	-1.2(2)	C8-C9-N3-C12	-173.74(14)
C42-C25-C26-N6	169.0(3)	C10-C9-N3-C12	-0.06(18)
C42A-C25-C26-N6	-162.0(3)	C13-C12-N3-C9	179.77(16)
C24-C25-C26-C27	174.1(2)	C11-C12-N3-C9	0.20(18)
C42-C25-C26-C27	-15.7(4)	C16-C17-N4-C14	1.4(2)
C42A-C25-C26-C27	13.4(5)	C18-C17-N4-C14	-175.21(16)
N1-C1-C27-C26	0.5(4)	C15-C14-N4-C17	-1.8(2)
C2-C1-C27-C26	176.3(2)	C13-C14-N4-C17	173.39(16)
N6-C26-C27-C1	2.4(4)	C19-C18-N5-C22	2.4(2)
C25-C26-C27-C1	-172.2(3)	C17-C18-N5-C22	-177.49(15)
C3-C2-C28-C29	-104.7(3)	C21-C22-N5-C18	-3.1(2)
C1-C2-C28-C29	80.7(4)	C23-C22-N5-C18	177.73(14)

C24-C23-N6-C26	-1.8(2)	C25-C26-N6-C23	1.9(2)
C22-C23-N6-C26	176.63(16)	C27-C26-N6-C23	-173.8(2)

Compound 4:

X-ray experimental for complex $(C_{42}H_{46}N_6)UO_2 \cdot 2 CHCl_3$ (contracted pyrihexaphyrin-uranyl complex **4**): Crystals grew as small clusters of dark red crystals by slow evaporation from dichloromethane: hexanes (1:1, v/v). The data crystal was cut from a group of crystals and had approximate dimensions; 0.16 x 0.04 x 0.03 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ -focus Cu K α radiation source ($\lambda = 1.5418 \text{ \AA}$) with collimating mirror monochromators. A total of 1060 frames of data were collected using ω -scans with a scan range of 1° and a counting time of 10 seconds per frame with a detector offset of $\pm 41.6^\circ$ and 42.5 seconds per frame with a detector offset of $\pm 112.0^\circ$. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Rigaku Oxford Diffraction's CrysAlisPro V 1.171.39.46.¹ The structure was solved by direct methods using SHELXT² and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.³ Structure analysis was aided by use of the programs PLATON⁴ and WinGX.⁵ The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

The function, $\sum w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0575 \cdot P)^2 + (8.1029 \cdot P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.116, with $R(F)$ equal to 0.0432 and a goodness of fit, S , = 1.03. Definitions used for calculating $R(F)$, $R_w(F^2)$ and the goodness of fit, S , are given below.⁶ The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁷ All figures were generated using SHELXTL/PC.⁸ Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found below.

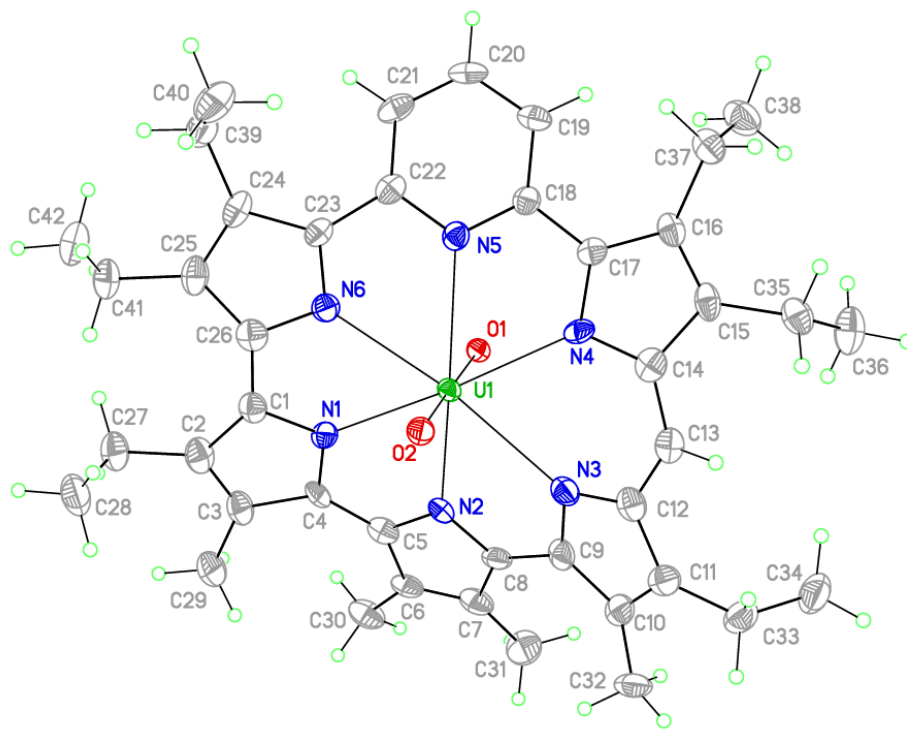


Figure S12. Structure of the contracted pyrihexaphyrin-uranyl complex **4** showing the atom-labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

Table 7. Crystal data and structure refinement for **4**.

Empirical formula	C ₄₄ H ₄₈ Cl ₆ N ₆ O ₂ U	
Formula weight	1143.61	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	a = 11.4660(3) Å	α = 90°.
	b = 14.7143(4) Å	β = 100.580(2)°.
	c = 27.0626(5) Å	γ = 90°.
Volume	4488.22(19) Å ³	
Z	4	
Density (calculated)	1.692 Mg/m ³	
Absorption coefficient	13.820 mm ⁻¹	
F(000)	2256	
Crystal size	0.160 x 0.040 x 0.030 mm ³	
Theta range for data collection	3.323 to 68.501°.	

Index ranges	-13<=h<=13, -12<=k<=17, -32<=l<=32
Reflections collected	25019
Independent reflections	8194 [R(int) = 0.0714]
Completeness to theta = 67.684°	99.6 %
Absorption correction	Gaussian and multi-scan
Max. and min. transmission	1.00 and 0.243
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8194 / 0 / 542
Goodness-of-fit on F ²	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0432, wR2 = 0.1072
R indices (all data)	R1 = 0.0538, wR2 = 0.1157
Extinction coefficient	n/a
Largest diff. peak and hole	2.066 and -1.246 e.Å ⁻³
CCDC number	1893883

Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C1	1393(6)	6214(5)	3738(3)	27(2)
C2	1118(6)	5343(6)	3939(3)	33(2)
C3	1238(6)	4701(5)	3588(3)	31(2)
C4	1615(6)	5186(5)	3172(3)	23(1)
C5	1995(6)	4934(5)	2737(3)	26(1)
C6	1968(6)	4126(5)	2425(3)	27(1)
C7	2620(7)	4317(5)	2072(3)	32(2)
C8	3093(6)	5229(5)	2179(3)	26(1)
C9	3939(7)	5795(5)	1995(2)	28(2)
C10	4884(6)	5562(6)	1745(2)	30(2)
C11	5489(6)	6345(5)	1724(3)	30(2)
C12	4878(6)	7037(5)	1948(2)	28(2)
C13	5085(6)	7959(5)	1914(3)	28(2)
C14	4386(6)	8665(5)	2016(2)	27(2)
C15	4454(6)	9567(5)	1824(2)	27(2)
C16	3566(6)	10064(5)	1957(2)	25(1)
C17	2967(6)	9447(5)	2243(2)	21(1)
C18	2071(6)	9647(5)	2534(2)	24(1)
C19	1381(6)	10453(5)	2475(3)	28(2)
C20	647(6)	10646(5)	2812(3)	30(2)
C21	628(6)	10061(5)	3203(3)	30(2)
C22	1251(6)	9255(5)	3231(2)	24(1)
C23	1210(6)	8563(5)	3600(2)	24(1)
C24	808(6)	8563(6)	4073(3)	31(2)
C25	894(6)	7676(6)	4246(3)	32(2)
C26	1306(6)	7153(5)	3862(3)	28(2)
C27	813(7)	5139(6)	4445(3)	39(2)
C28	1942(8)	5023(7)	4850(3)	45(2)
C29	1115(8)	3696(6)	3634(3)	43(2)
C30	1260(7)	3262(5)	2455(3)	36(2)
C31	2733(9)	3723(6)	1633(3)	45(2)

C32	5207(7)	4660(6)	1547(3)	37(2)
C33	6569(6)	6495(6)	1483(3)	35(2)
C34	6255(8)	6735(7)	923(3)	47(2)
C35	5297(7)	9856(5)	1483(3)	31(2)
C36	4846(8)	9601(7)	933(3)	43(2)
C37	3286(7)	11040(5)	1827(3)	31(2)
C38	2300(8)	11153(6)	1365(3)	42(2)
C39	452(7)	9368(6)	4357(3)	38(2)
C40	1468(8)	10041(7)	4530(3)	46(2)
C41	648(7)	7386(6)	4751(3)	35(2)
C42	-660(8)	7284(7)	4767(3)	43(2)
C43	2027(8)	7342(7)	1153(3)	48(2)
C44	4731(10)	7641(9)	4419(4)	63(3)
N1	1726(5)	6090(4)	3282(2)	22(1)
N2	2624(5)	5614(4)	2550(2)	23(1)
N3	3929(5)	6678(4)	2131(2)	26(1)
N4	3440(5)	8597(4)	2280(2)	22(1)
N5	1961(5)	9036(4)	2890(2)	23(1)
N6	1532(5)	7728(4)	3486(2)	24(1)
O1	1299(4)	7323(3)	2302(2)	21(1)
O2	3951(4)	7288(3)	3234(2)	24(1)
U1	2608(1)	7285(1)	2772(1)	18(1)
CL1	2988(2)	6885(3)	785(1)	76(1)
CL2	646(2)	6766(2)	1048(1)	47(1)
CL3	1809(2)	8509(2)	1028(1)	51(1)
CL4	4360(4)	6728(3)	4779(2)	102(1)
CL5	4074(3)	8608(3)	4602(1)	85(1)
CL6	6242(3)	7759(3)	4482(2)	110(2)

Table 9. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for **4**.

C1-N1	1.368(9)	C2-C27	1.505(10)
C1-C26	1.430(11)	C3-C4	1.463(9)
C1-C2	1.449(11)	C3-C29	1.493(12)
C2-C3	1.365(12)	C4-N1	1.364(9)

C4-C5	1.381(10)	C22-C23	1.435(10)
C5-N2	1.383(9)	C23-N6	1.336(9)
C5-C6	1.455(10)	C23-C24	1.437(9)
C6-C7	1.346(11)	C24-C25	1.383(12)
C6-C30	1.518(10)	C24-C39	1.507(11)
C7-C8	1.457(10)	C25-C26	1.440(11)
C7-C31	1.499(11)	C25-C41	1.507(10)
C8-N2	1.350(9)	C26-N6	1.384(10)
C8-C9	1.436(11)	C27-C28	1.545(11)
C9-N3	1.351(10)	C27-H27A	0.99
C9-C10	1.419(10)	C27-H27B	0.99
C10-C11	1.351(11)	C28-H28A	0.98
C10-C32	1.504(11)	C28-H28B	0.98
C11-C12	1.433(11)	C28-H28C	0.98
C11-C33	1.517(10)	C29-H29A	0.98
C12-N3	1.381(9)	C29-H29B	0.98
C12-C13	1.384(11)	C29-H29C	0.98
C13-C14	1.371(11)	C30-H30A	0.98
C13-H13	0.95	C30-H30B	0.98
C14-N4	1.408(9)	C30-H30C	0.98
C14-C15	1.432(11)	C31-H31A	0.98
C15-C16	1.355(11)	C31-H31B	0.98
C15-C35	1.514(10)	C31-H31C	0.98
C16-C17	1.445(10)	C32-H32A	0.98
C16-C37	1.499(10)	C32-H32B	0.98
C17-N4	1.359(9)	C32-H32C	0.98
C17-C18	1.436(9)	C33-C34	1.535(11)
C18-N5	1.341(9)	C33-H33A	0.99
C18-C19	1.418(10)	C33-H33B	0.99
C19-C20	1.381(11)	C34-H34A	0.98
C19-H19	0.95	C34-H34B	0.98
C20-C21	1.367(11)	C34-H34C	0.98
C20-H20	0.95	C35-C36	1.532(10)
C21-C22	1.378(11)	C35-H35A	0.99
C21-H21	0.95	C35-H35B	0.99
C22-N5	1.375(8)	C36-H36A	0.98

C36-H36B	0.98	C42-H42B	0.98
C36-H36C	0.98	C42-H42C	0.98
C37-C38	1.532(10)	C43-CL1	1.749(9)
C37-H37A	0.99	C43-CL3	1.758(11)
C37-H37B	0.99	C43-CL2	1.773(10)
C38-H38A	0.98	C43-H43	1.00
C38-H38B	0.98	C44-CL6	1.719(12)
C38-H38C	0.98	C44-CL5	1.724(12)
C39-C40	1.535(12)	C44-CL4	1.758(13)
C39-H39A	0.99	C44-H44	1.00
C39-H39B	0.99	N1-U1	2.557(6)
C40-H40A	0.98	N2-U1	2.531(6)
C40-H40B	0.98	N3-U1	2.657(6)
C40-H40C	0.98	N4-U1	2.622(6)
C41-C42	1.516(11)	N5-U1	2.717(6)
C41-H41A	0.99	N6-U1	2.561(6)
C41-H41B	0.99	O1-U1	1.780(5)
C42-H42A	0.98	O2-U1	1.798(5)
N1-C1-C26	112.5(6)	C5-C6-C30	127.4(7)
N1-C1-C2	109.7(7)	C6-C7-C8	106.6(7)
C26-C1-C2	137.5(7)	C6-C7-C31	125.5(7)
C3-C2-C1	107.1(6)	C8-C7-C31	127.6(7)
C3-C2-C27	124.4(8)	N2-C8-C9	113.7(6)
C1-C2-C27	128.4(8)	N2-C8-C7	110.5(7)
C2-C3-C4	106.2(7)	C9-C8-C7	135.8(7)
C2-C3-C29	127.3(7)	N3-C9-C10	114.1(7)
C4-C3-C29	126.3(7)	N3-C9-C8	115.0(6)
N1-C4-C5	114.7(6)	C10-C9-C8	130.4(7)
N1-C4-C3	109.7(6)	C11-C10-C9	104.9(7)
C5-C4-C3	135.2(7)	C11-C10-C32	125.1(7)
C4-C5-N2	112.6(6)	C9-C10-C32	130.0(8)
C4-C5-C6	137.7(7)	C10-C11-C12	107.0(7)
N2-C5-C6	109.7(6)	C10-C11-C33	127.5(7)
C7-C6-C5	106.6(6)	C12-C11-C33	125.4(7)
C7-C6-C30	125.8(7)	N3-C12-C13	123.8(7)

N3-C12-C11	111.0(7)	C25-C24-C39	125.4(7)
C13-C12-C11	124.4(7)	C23-C24-C39	127.9(8)
C14-C13-C12	128.0(7)	C24-C25-C26	105.9(6)
C14-C13-H13	116.0	C24-C25-C41	124.0(7)
C12-C13-H13	116.0	C26-C25-C41	130.0(8)
C13-C14-N4	125.6(7)	N6-C26-C1	112.8(6)
C13-C14-C15	123.8(7)	N6-C26-C25	109.5(6)
N4-C14-C15	110.4(6)	C1-C26-C25	137.0(7)
C16-C15-C14	108.0(6)	C2-C27-C28	111.3(7)
C16-C15-C35	127.2(7)	C2-C27-H27A	109.4
C14-C15-C35	124.4(7)	C28-C27-H27A	109.4
C15-C16-C17	104.9(6)	C2-C27-H27B	109.4
C15-C16-C37	126.4(7)	C28-C27-H27B	109.4
C17-C16-C37	128.7(7)	H27A-C27-H27B	108.0
N4-C17-C18	117.6(6)	C27-C28-H28A	109.5
N4-C17-C16	113.3(6)	C27-C28-H28B	109.5
C18-C17-C16	128.6(6)	H28A-C28-H28B	109.5
N5-C18-C19	121.2(6)	C27-C28-H28C	109.5
N5-C18-C17	115.4(6)	H28A-C28-H28C	109.5
C19-C18-C17	123.3(7)	H28B-C28-H28C	109.5
C20-C19-C18	119.4(7)	C3-C29-H29A	109.5
C20-C19-H19	120.3	C3-C29-H29B	109.5
C18-C19-H19	120.3	H29A-C29-H29B	109.5
C21-C20-C19	118.7(7)	C3-C29-H29C	109.5
C21-C20-H20	120.6	H29A-C29-H29C	109.5
C19-C20-H20	120.6	H29B-C29-H29C	109.5
C20-C21-C22	120.1(7)	C6-C30-H30A	109.5
C20-C21-H21	119.9	C6-C30-H30B	109.5
C22-C21-H21	119.9	H30A-C30-H30B	109.5
N5-C22-C21	122.0(7)	C6-C30-H30C	109.5
N5-C22-C23	113.6(6)	H30A-C30-H30C	109.5
C21-C22-C23	124.4(6)	H30B-C30-H30C	109.5
N6-C23-C22	116.4(6)	C7-C31-H31A	109.5
N6-C23-C24	110.8(7)	C7-C31-H31B	109.5
C22-C23-C24	132.7(7)	H31A-C31-H31B	109.5
C25-C24-C23	106.6(7)	C7-C31-H31C	109.5

H31A-C31-H31C	109.5	C38-C37-H37B	109.0
H31B-C31-H31C	109.5	H37A-C37-H37B	107.8
C10-C32-H32A	109.5	C37-C38-H38A	109.5
C10-C32-H32B	109.5	C37-C38-H38B	109.5
H32A-C32-H32B	109.5	H38A-C38-H38B	109.5
C10-C32-H32C	109.5	C37-C38-H38C	109.5
H32A-C32-H32C	109.5	H38A-C38-H38C	109.5
H32B-C32-H32C	109.5	H38B-C38-H38C	109.5
C11-C33-C34	113.3(6)	C24-C39-C40	113.7(7)
C11-C33-H33A	108.9	C24-C39-H39A	108.8
C34-C33-H33A	108.9	C40-C39-H39A	108.8
C11-C33-H33B	108.9	C24-C39-H39B	108.8
C34-C33-H33B	108.9	C40-C39-H39B	108.8
H33A-C33-H33B	107.7	H39A-C39-H39B	107.7
C33-C34-H34A	109.5	C39-C40-H40A	109.5
C33-C34-H34B	109.5	C39-C40-H40B	109.5
H34A-C34-H34B	109.5	H40A-C40-H40B	109.5
C33-C34-H34C	109.5	C39-C40-H40C	109.5
H34A-C34-H34C	109.5	H40A-C40-H40C	109.5
H34B-C34-H34C	109.5	H40B-C40-H40C	109.5
C15-C35-C36	112.6(6)	C25-C41-C42	113.9(7)
C15-C35-H35A	109.1	C25-C41-H41A	108.8
C36-C35-H35A	109.1	C42-C41-H41A	108.8
C15-C35-H35B	109.1	C25-C41-H41B	108.8
C36-C35-H35B	109.1	C42-C41-H41B	108.8
H35A-C35-H35B	107.8	H41A-C41-H41B	107.7
C35-C36-H36A	109.5	C41-C42-H42A	109.5
C35-C36-H36B	109.5	C41-C42-H42B	109.5
H36A-C36-H36B	109.5	H42A-C42-H42B	109.5
C35-C36-H36C	109.5	C41-C42-H42C	109.5
H36A-C36-H36C	109.5	H42A-C42-H42C	109.5
H36B-C36-H36C	109.5	H42B-C42-H42C	109.5
C16-C37-C38	112.9(6)	CL1-C43-CL3	110.4(5)
C16-C37-H37A	109.0	CL1-C43-CL2	111.3(6)
C38-C37-H37A	109.0	CL3-C43-CL2	110.2(5)
C16-C37-H37B	109.0	CL1-C43-H43	108.3

CL3-C43-H43	108.3	O1-U1-N2	84.47(19)
CL2-C43-H43	108.3	O2-U1-N2	97.17(19)
CL6-C44-CL5	111.9(7)	O1-U1-N1	92.39(19)
CL6-C44-CL4	111.4(7)	O2-U1-N1	89.92(19)
CL5-C44-CL4	108.0(6)	N2-U1-N1	58.72(17)
CL6-C44-H44	108.5	O1-U1-N6	94.03(19)
CL5-C44-H44	108.5	O2-U1-N6	86.8(2)
CL4-C44-H44	108.5	N2-U1-N6	116.84(18)
C4-N1-C1	107.3(6)	N1-U1-N6	58.27(18)
C4-N1-U1	125.6(4)	O1-U1-N4	87.28(18)
C1-N1-U1	126.8(5)	O2-U1-N4	90.39(19)
C8-N2-C5	105.8(6)	N2-U1-N4	125.17(17)
C8-N2-U1	127.3(5)	N1-U1-N4	176.00(17)
C5-N2-U1	126.2(5)	N6-U1-N4	117.77(17)
C9-N3-C12	102.9(6)	O1-U1-N3	93.00(19)
C9-N3-U1	122.5(5)	O2-U1-N3	86.40(19)
C12-N3-U1	133.3(5)	N2-U1-N3	59.28(18)
C17-N4-C14	103.4(6)	N1-U1-N3	116.79(18)
C17-N4-U1	122.5(4)	N6-U1-N3	171.57(18)
C14-N4-U1	134.1(5)	N4-U1-N3	67.21(17)
C18-N5-C22	118.0(6)	O1-U1-N5	80.89(18)
C18-N5-U1	119.2(4)	O2-U1-N5	97.62(18)
C22-N5-U1	120.7(5)	N2-U1-N5	164.41(17)
C23-N6-C26	107.1(6)	N1-U1-N5	116.40(17)
C23-N6-U1	127.0(5)	N6-U1-N5	59.29(17)
C26-N6-U1	125.5(5)	N4-U1-N5	59.61(16)
O1-U1-O2	177.6(2)	N3-U1-N5	126.64(17)

Table 10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C1	22(3)	32(4)	24(3)	3(3)	2(3)	0(3)
C2	25(3)	41(5)	32(4)	6(3)	6(3)	-7(3)
C3	30(4)	34(4)	30(4)	7(3)	7(3)	-6(3)
C4	25(3)	17(3)	26(3)	8(3)	3(3)	-2(2)
C5	25(3)	22(4)	27(3)	0(3)	-5(3)	-1(3)
C6	32(3)	14(3)	32(3)	-1(3)	-1(3)	2(3)
C7	41(4)	18(4)	35(4)	0(3)	-1(3)	1(3)
C8	33(4)	17(4)	25(3)	0(3)	2(3)	8(3)
C9	39(4)	29(4)	15(3)	1(3)	2(3)	1(3)
C10	30(3)	39(5)	19(3)	0(3)	2(3)	5(3)
C11	31(4)	34(4)	22(3)	-2(3)	0(3)	6(3)
C12	28(3)	34(4)	18(3)	3(3)	-3(3)	-1(3)
C13	26(3)	35(4)	24(3)	1(3)	5(3)	-4(3)
C14	24(3)	35(4)	19(3)	-4(3)	-3(2)	-2(3)
C15	35(4)	28(4)	17(3)	-1(3)	4(3)	-13(3)
C16	31(3)	22(4)	20(3)	-1(3)	2(3)	-9(3)
C17	22(3)	21(4)	18(3)	-6(3)	0(2)	-2(3)
C18	28(3)	24(4)	18(3)	-3(3)	2(2)	1(3)
C19	32(4)	18(4)	30(3)	-1(3)	0(3)	4(3)
C20	28(3)	19(4)	39(4)	-7(3)	0(3)	9(3)
C21	30(3)	31(4)	29(3)	-16(3)	2(3)	1(3)
C22	22(3)	26(4)	25(3)	-7(3)	4(3)	-5(3)
C23	26(3)	26(4)	23(3)	-5(3)	7(3)	0(3)
C24	31(4)	42(5)	23(3)	-9(3)	10(3)	-4(3)
C25	28(3)	45(5)	26(3)	2(3)	9(3)	-8(3)
C26	21(3)	34(4)	28(3)	1(3)	-1(3)	-1(3)
C27	40(4)	45(5)	33(4)	8(4)	13(3)	-7(4)
C28	53(5)	53(6)	30(4)	13(4)	8(4)	2(4)
C29	54(5)	34(5)	43(4)	12(4)	18(4)	-2(4)
C30	41(4)	19(4)	42(4)	0(3)	-5(3)	-4(3)
C31	63(6)	35(5)	38(4)	-12(4)	12(4)	0(4)

C32	42(4)	34(5)	34(4)	0(3)	0(3)	20(3)
C33	27(3)	46(5)	34(4)	0(3)	8(3)	8(3)
C34	46(5)	65(7)	33(4)	3(4)	19(4)	9(4)
C35	35(4)	27(4)	32(4)	3(3)	5(3)	-8(3)
C36	42(4)	60(6)	26(4)	1(4)	9(3)	-13(4)
C37	44(4)	27(4)	21(3)	-2(3)	0(3)	-5(3)
C38	61(5)	32(5)	29(4)	4(3)	1(4)	4(4)
C39	46(4)	38(5)	31(4)	-5(3)	13(3)	-1(4)
C40	53(5)	47(6)	39(4)	-19(4)	12(4)	-3(4)
C41	38(4)	48(5)	20(3)	1(3)	6(3)	-4(3)
C42	43(5)	58(6)	29(4)	-5(4)	13(3)	-10(4)
C43	42(5)	86(8)	17(3)	6(4)	5(3)	22(5)
C44	60(6)	96(9)	29(4)	-9(5)	-3(4)	2(6)
N1	26(3)	24(3)	16(2)	-4(2)	1(2)	2(2)
N2	26(3)	21(3)	22(3)	6(2)	3(2)	4(2)
N3	35(3)	22(3)	21(3)	2(2)	3(2)	1(2)
N4	24(3)	20(3)	21(2)	-7(2)	3(2)	3(2)
N5	23(3)	27(3)	19(2)	0(2)	3(2)	1(2)
N6	24(3)	23(3)	25(3)	0(2)	6(2)	-1(2)
O1	27(2)	17(2)	18(2)	1(2)	5(2)	2(2)
O2	31(2)	18(3)	24(2)	-1(2)	9(2)	-1(2)
U1	23(1)	14(1)	16(1)	0(1)	3(1)	1(1)
CL1	54(1)	141(3)	31(1)	-9(1)	0(1)	44(2)
CL2	74(1)	35(1)	33(1)	2(1)	14(1)	-8(1)
CL3	55(1)	59(1)	36(1)	4(1)	-3(1)	-19(1)
CL4	125(3)	78(2)	97(2)	9(2)	5(2)	-37(2)
CL5	92(2)	109(3)	63(2)	36(2)	38(2)	43(2)
CL6	58(2)	185(4)	96(2)	76(3)	41(2)	39(2)

Table 11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for **4**.

	x	y	z	U(eq)
H13	5801	8124	1807	34
H19	1423	10857	2205	33
H20	164	11175	2774	36
H21	185	10209	3456	36
H27A	336	4574	4423	46
H27B	326	5640	4543	46
H28A	2410	4513	4760	68
H28B	1717	4904	5176	68
H28C	2416	5581	4871	68
H29A	1070	3540	3982	64
H29B	1805	3395	3539	64
H29C	391	3492	3410	64
H30A	1079	2978	2122	54
H30B	519	3410	2569	54
H30C	1726	2840	2693	54
H31A	3375	3284	1734	67
H31B	2914	4100	1358	67
H31C	1986	3399	1519	67
H32A	4732	4558	1212	56
H32B	5049	4175	1774	56
H32C	6051	4658	1526	56
H33A	7059	5936	1523	42
H33B	7053	6992	1663	42
H34A	5768	6249	742	70
H34B	6985	6802	786	70
H34C	5810	7307	881	70
H35A	6078	9566	1599	38
H35B	5410	10523	1509	38
H36A	4724	8943	905	64
H36B	5432	9784	730	64
H36C	4093	9913	810	64
H37A	4013	11345	1763	37

H37B	3042	11344	2118	37
H38A	2559	10893	1070	62
H38B	2127	11801	1308	62
H38C	1584	10839	1423	62
H39A	151	9146	4655	45
H39B	-205	9692	4138	45
H40A	2099	9738	4765	69
H40B	1169	10559	4697	69
H40C	1783	10256	4238	69
H41A	997	7839	5006	43
H41B	1048	6797	4843	43
H42A	-1060	7870	4689	64
H42B	-753	7087	5104	64
H42C	-1013	6831	4519	64
H43	2401	7269	1515	58
H44	4394	7520	4057	76

Table 12. Torsion angles [°] for **4**.

N1-C1-C2-C3	-2.7(8)	C4-C5-C6-C7	-173.7(8)
C26-C1-C2-C3	169.9(8)	N2-C5-C6-C7	2.6(8)
N1-C1-C2-C27	174.5(7)	C4-C5-C6-C30	11.3(13)
C26-C1-C2-C27	-12.9(14)	N2-C5-C6-C30	-172.3(7)
C1-C2-C3-C4	1.2(8)	C5-C6-C7-C8	2.4(8)
C27-C2-C3-C4	-176.2(7)	C30-C6-C7-C8	177.5(7)
C1-C2-C3-C29	176.2(8)	C5-C6-C7-C31	-172.8(7)
C27-C2-C3-C29	-1.1(13)	C30-C6-C7-C31	2.2(13)
C2-C3-C4-N1	0.7(8)	C6-C7-C8-N2	-7.0(8)
C29-C3-C4-N1	-174.4(7)	C31-C7-C8-N2	168.2(8)
C2-C3-C4-C5	172.2(8)	C6-C7-C8-C9	171.3(8)
C29-C3-C4-C5	-2.9(14)	C31-C7-C8-C9	-13.5(14)
N1-C4-C5-N2	11.8(8)	N2-C8-C9-N3	-14.8(9)
C3-C4-C5-N2	-159.4(7)	C7-C8-C9-N3	166.9(7)
N1-C4-C5-C6	-171.9(7)	N2-C8-C9-C10	156.3(7)
C3-C4-C5-C6	16.9(14)	C7-C8-C9-C10	-22.0(13)

N3-C9-C10-C11	-0.4(8)	C20-C21-C22-N5	4.0(10)
C8-C9-C10-C11	-171.6(7)	C20-C21-C22-C23	-174.6(7)
N3-C9-C10-C32	178.7(7)	N5-C22-C23-N6	-19.8(9)
C8-C9-C10-C32	7.6(12)	C21-C22-C23-N6	158.9(6)
C9-C10-C11-C12	-1.5(7)	N5-C22-C23-C24	165.1(7)
C32-C10-C11-C12	179.3(6)	C21-C22-C23-C24	-16.2(12)
C9-C10-C11-C33	-178.3(7)	N6-C23-C24-C25	-0.3(8)
C32-C10-C11-C33	2.6(12)	C22-C23-C24-C25	175.1(7)
C10-C11-C12-N3	2.9(8)	N6-C23-C24-C39	175.2(7)
C33-C11-C12-N3	179.8(6)	C22-C23-C24-C39	-9.5(13)
C10-C11-C12-C13	-167.2(7)	C23-C24-C25-C26	-2.1(8)
C33-C11-C12-C13	9.6(11)	C39-C24-C25-C26	-177.7(7)
N3-C12-C13-C14	-4.8(11)	C23-C24-C25-C41	175.2(7)
C11-C12-C13-C14	164.2(7)	C39-C24-C25-C41	-0.4(12)
C12-C13-C14-N4	14.7(11)	N1-C1-C26-N6	2.3(8)
C12-C13-C14-C15	-159.1(7)	C2-C1-C26-N6	-170.1(8)
C13-C14-C15-C16	174.1(6)	N1-C1-C26-C25	172.0(8)
N4-C14-C15-C16	-0.6(8)	C2-C1-C26-C25	-0.4(15)
C13-C14-C15-C35	0.4(11)	C24-C25-C26-N6	3.8(8)
N4-C14-C15-C35	-174.3(6)	C41-C25-C26-N6	-173.3(7)
C14-C15-C16-C17	1.0(7)	C24-C25-C26-C1	-166.1(8)
C35-C15-C16-C17	174.5(6)	C41-C25-C26-C1	16.8(14)
C14-C15-C16-C37	-178.7(6)	C3-C2-C27-C28	92.6(10)
C35-C15-C16-C37	-5.3(11)	C1-C2-C27-C28	-84.1(10)
C15-C16-C17-N4	-1.2(8)	C10-C11-C33-C34	87.6(10)
C37-C16-C17-N4	178.6(6)	C12-C11-C33-C34	-88.6(9)
C15-C16-C17-C18	170.2(6)	C16-C15-C35-C36	-91.7(9)
C37-C16-C17-C18	-10.0(11)	C14-C15-C35-C36	80.7(9)
N4-C17-C18-N5	13.0(9)	C15-C16-C37-C38	96.9(9)
C16-C17-C18-N5	-158.1(6)	C17-C16-C37-C38	-82.8(9)
N4-C17-C18-C19	-170.2(6)	C25-C24-C39-C40	111.2(9)
C16-C17-C18-C19	18.8(11)	C23-C24-C39-C40	-63.4(11)
N5-C18-C19-C20	4.9(10)	C24-C25-C41-C42	79.8(10)
C17-C18-C19-C20	-171.8(6)	C26-C25-C41-C42	-103.6(10)
C18-C19-C20-C21	1.5(11)	C5-C4-N1-C1	-175.8(6)
C19-C20-C21-C22	-5.7(11)	C3-C4-N1-C1	-2.4(7)

C5-C4-N1-U1	-1.8(8)	C16-C17-N4-C14	0.8(7)
C3-C4-N1-U1	171.6(4)	C18-C17-N4-U1	7.3(8)
C26-C1-N1-C4	-171.5(6)	C16-C17-N4-U1	179.7(4)
C2-C1-N1-C4	3.1(8)	C13-C14-N4-C17	-174.7(6)
C26-C1-N1-U1	14.6(8)	C15-C14-N4-C17	-0.1(7)
C2-C1-N1-U1	-170.8(4)	C13-C14-N4-U1	6.6(10)
C9-C8-N2-C5	-170.3(6)	C15-C14-N4-U1	-178.9(4)
C7-C8-N2-C5	8.4(7)	C19-C18-N5-C22	-6.7(9)
C9-C8-N2-U1	18.7(8)	C17-C18-N5-C22	170.3(6)
C7-C8-N2-U1	-162.6(4)	C19-C18-N5-U1	156.7(5)
C4-C5-N2-C8	170.5(6)	C17-C18-N5-U1	-26.4(7)
C6-C5-N2-C8	-6.8(7)	C21-C22-N5-C18	2.3(10)
C4-C5-N2-U1	-18.4(8)	C23-C22-N5-C18	-179.0(6)
C6-C5-N2-U1	164.3(4)	C21-C22-N5-U1	-160.8(5)
C10-C9-N3-C12	2.1(8)	C23-C22-N5-U1	18.0(7)
C8-C9-N3-C12	174.7(6)	C22-C23-N6-C26	-173.5(6)
C10-C9-N3-U1	-166.3(4)	C24-C23-N6-C26	2.6(8)
C8-C9-N3-U1	6.3(8)	C22-C23-N6-U1	13.6(9)
C13-C12-N3-C9	167.2(6)	C24-C23-N6-U1	-170.3(4)
C11-C12-N3-C9	-3.0(7)	C1-C26-N6-C23	168.6(6)
C13-C12-N3-U1	-26.3(10)	C25-C26-N6-C23	-4.0(8)
C11-C12-N3-U1	163.5(4)	C1-C26-N6-U1	-18.4(8)
C18-C17-N4-C14	-171.6(6)	C25-C26-N6-U1	169.1(4)

References & Notes

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- 6) $R_w(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w(|F_o|^4)\}^{1/2}$ where w is the weight given each reflection.
 $R(F) = \sum (|F_o| - |F_c|) / \sum |F_o|$ for reflections with $F_o > 4(\sigma(F_o))$.
 $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.
- 7) A. J. C. Wilson, *International Tables for X-ray Crystallography Vol. C*. Boston: Kluwer Academic Press, 1992, Tables 4.2.6.8 and 6.1.1.4.
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