Electronic Supporting Information (ESI)

for

Bimetallic Uranyl/Cobalt(II) Isothiocyanates: Structure, Property and Spectroscopic Analysis of Homo- and Heterometallic Phases

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Table of Contents

Table S1: Crystallography table for compounds **1-3**.

	1	**2**	**3**
Chemical Formula	$(C_4H_{12}N)_3[UO_2(NCS)_5]$	$(C_4H_{12}N)_2[Co(NCS)_4]$	$(C_4H_{12}N)_5[UO_2(NCS)_5][Co(NCS)_4]$
Formula Weight (g/mol)	782.9	439.5	1222.4
Crystal System	Monoclinic	Triclinic	Monoclinic
Space Group	$P2_1/c$	P-1	$P2_1/c$
a (Å)	16.377(1)	11.104(2)	16.828(1)
b (Å)	9.279(1)	13.285(2)	14.910(1)
c (Å)	20.365(2)	24.380(4)	21.455(2)
α (°)	90	95.465(5)	90
β (°)	97.732(3)	90.187(6)	102.888(3)
γ (°)	90	114.197(5)	90
V (Å^3)	3066.5(5)	3261.8(8)	5247.0(7)
Z	4	6	4
T (K)	100(2)	100(2)	100(2)
λ (Mo Kα)	0.71073	0.71073	0.71073
μ (mm^{-1})	5.661	1.179	3.797
R_{int}	0.0867	0.0392	0.0904
R_1	0.0231	0.0344	0.0379
wR2	0.0429	0.0831	0.0973

Figure S1: ORTEP drawing of compound **1**, $(C_4H_{12}N)_3[UO_2(NCS)_5]$.

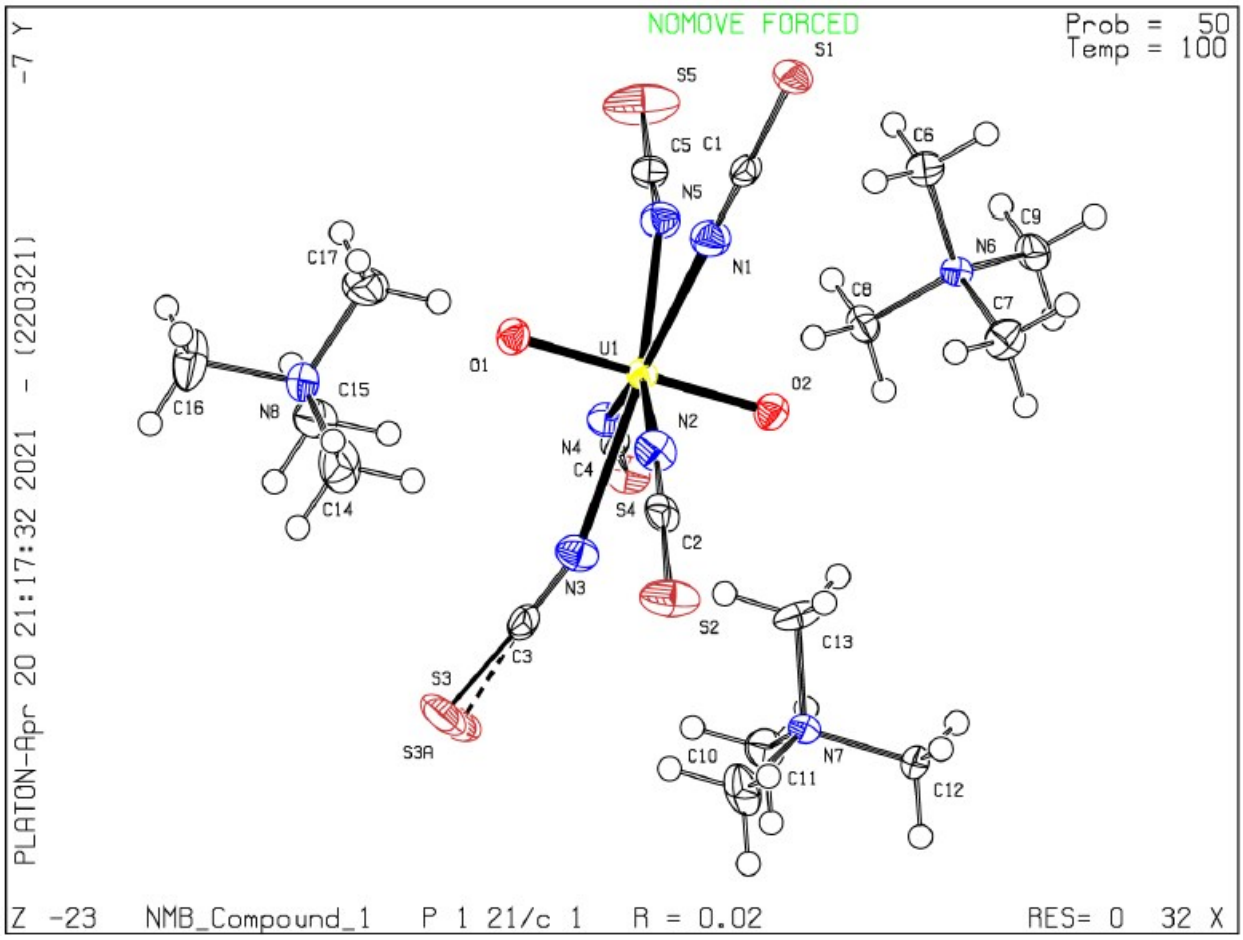

Table S2: Bond distances and angles for compound **1**, $(C_4H_{12}N)_3[UO_2(NCS)_5]$

Atom 1-Atom 2	Bond Length (Å)	Atom 1-Atom 2-Atom 3	Bond Angle (°)
U(1)-O(1)	1.765(2)	O(1)-U(1)-O(2)	179.81(11)
U(1)-O(2)	1.768(2)	O(1)-U(1)-N(5)	88.52(10)
U(1)-N(5)	2.421(3)	O(2)-U(1)-N(5)	91.29(10)
U(1)-N(2)	2.424(3)	O(1)-U(1)-N(2)	90.47(10)
U(1)-N(1)	2.446(3)	O(2)-U(1)-N(2)	89.69(10)
U(1)-N(3)	2.458(3)	N(5)-U(1)-N(2)	147.46(9)
U(1)-N(4)	2.482(3)	O(1)-U(1)-N(1)	91.76(10)
S(4)-C(4)	1.629(3)	O(2)-U(1)-N(1)	88.18(10)
S(1)-C(1)	1.622(3)	N(5)-U(1)-N(1)	73.65(9)
S(5)-C(5)	1.616(4)	N(2)-U(1)-N(1)	73.87(9)
N(6)-C(7)	1.492(4)	O(1)-U(1)-N(3)	87.06(10)
N(6)-C(9)	1.495(4)	O(2)-U(1)-N(3)	93.10(10)
N(6)-C(8)	1.498(4)	N(5)-U(1)-N(3)	140.24(9)
N(6)-C(6)	1.499(4)	N(2)-U(1)-N(3)	72.11(9)
N(7)-C(10)	1.492(4)	N(1)-U(1)-N(3)	145.95(9)
N(7)-C(11)	1.493(4)	O(1)-U(1)-N(4)	93.92(9)
N(7)-C(13)	1.495(4)	O(2)-U(1)-N(4)	86.03(9)
N(7)-C(12)	1.498(4)	N(5)-U(1)-N(4)	70.69(9)
N(8)-C(17)	1.491(4)	N(2)-U(1)-N(4)	141.77(9)
N(8)-C(15)	1.493(4)	N(1)-U(1)-N(4)	143.70(9)
N(8)-C(14)	1.493(5)	N(3)-U(1)-N(4)	70.23(9)
N(8)-C(16)	1.497(4)	C(7)-N(6)-C(9)	109.6(2)
N(2)-C(2)	1.167(4)	C(7)-N(6)-C(8)	109.6(3)
N(4)-C(4)	1.165(4)	C(9)-N(6)-C(8)	108.9(2)
N(3)-C(3)	1.149(4)	C(7)-N(6)-C(6)	109.9(2)
N(1)-C(1)	1.160(4)	C(9)-N(6)-C(6)	109.5(2)
N(5)-C(5)	1.152(4)	C(8)-N(6)-C(6)	109.4(2)
C(3)-S(3)	1.588(6)	C(10)-N(7)-C(11)	110.1(3)
C(3)-S(3A)	1.702(8)	C(10)-N(7)-C(13)	110.0(3)
C(2)-S(2)	1.615(4)	C(11)-N(7)-C(13)	109.7(3)
		C(10)-N(7)-C(12)	108.7(3)
		C(11)-N(7)-C(12)	109.4(3)
		C(13)-N(7)-C(12)	109.0(2)
		C(17)-N(8)-C(15)	108.4(3)
		C(17)-N(8)-C(14)	110.2(3)
		C(15)-N(8)-C(14)	108.8(3)
		C(17)-N(8)-C(16)	110.5(3)
		C(15)-N(8)-C(16)	108.5(3)
		C(14)-N(8)-C(16)	110.4(3)
		C(2)-N(2)-U(1)	160.5(3)
		C(4)-N(4)-U(1)	163.3(2)
		C(3)-N(3)-U(1)	160.3(3)
		C(1)-N(1)-U(1)	176.3(3)
		C(5)-N(5)-U(1)	154.2(3)
		N(1)-C(1)-S(1)	178.8(3)
		N(5)-C(5)-S(5)	177.2(3)
		N(4)-C(4)-S(4)	179.8(3)
		N(3)-C(3)-S(3)	171.2(13)
		N(3)-C(3)-S(3A)	166.9(7)
		N(2)-C(2)-S(2)	179.1(3)

Figure S2: ORTEP drawing of compound **2**, $(C_4H_{12}N)_2[Co(NCS)_4]$.

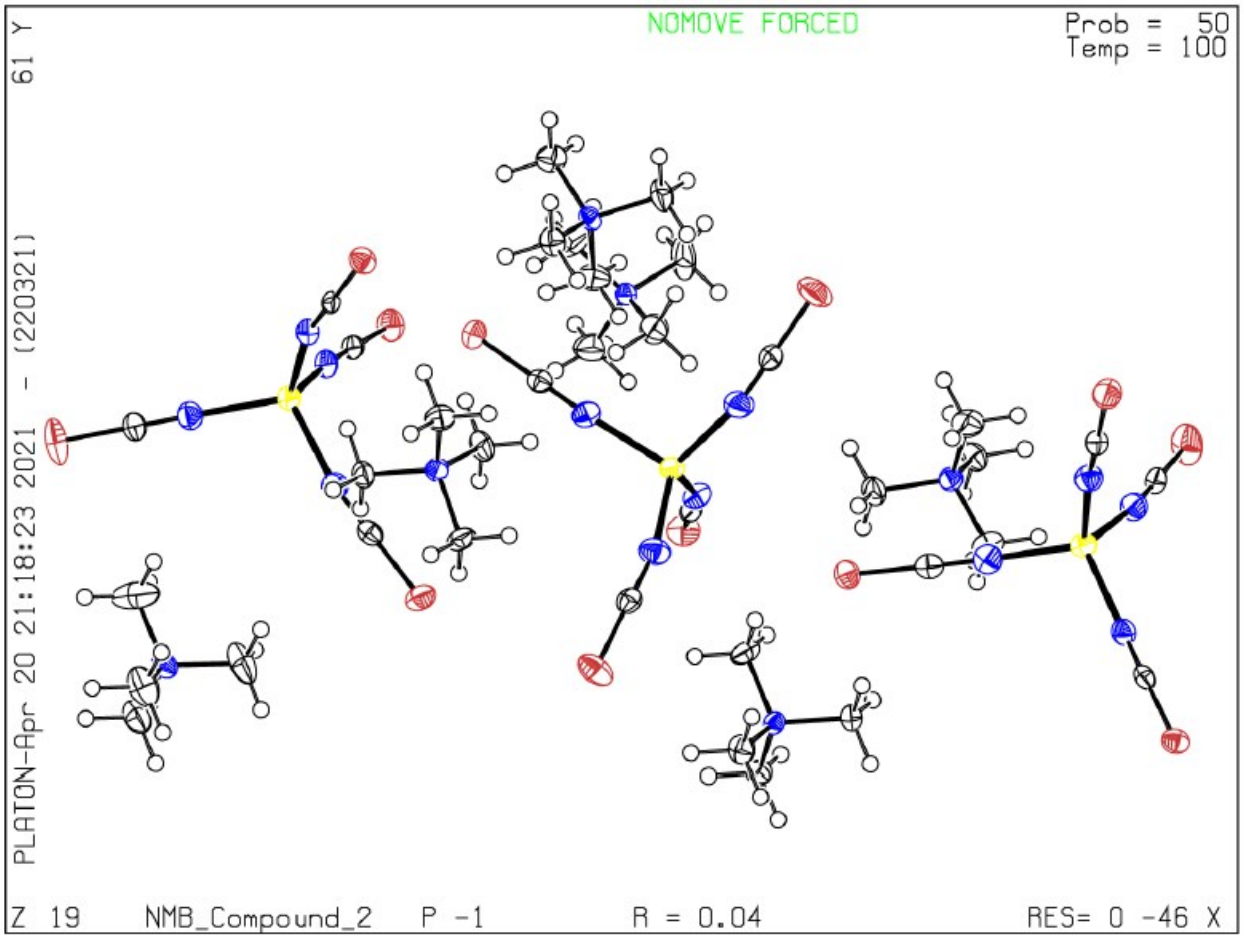

Table S3: Bond distances and angles for compound **2**, $(C_4H_{12}N)_2[Co(NCS)_4]$.

Atom 1-Atom 2	Bond Length (Å)	Atom 1-Atom 2-Atom 3	Bond Angle (°)
Co(2)-N(6)	1.928(3)	N(6)-Co(2)-N(8)	115.15(12)
Co(2)-N(8)	1.935(3)	N(6)-Co(2)-N(5)	113.01(13)
Co(2)-N(5)	1.960(3)	N(8)-Co(2)-N(5)	107.82(12)
Co(2)-N(7)	1.963(3)	N(6)-Co(2)-N(7)	106.60(12)
Co(3)-N(9)	1.960(3)	N(8)-Co(2)-N(7)	111.07(13)
Co(3)-N(11)	1.964(3)	N(5)-Co(2)-N(7)	102.49(10)
Co(3)-N(10)	1.968(3)	N(9)-Co(3)-N(11)	107.10(12)
Co(3)-N(12)	1.976(3)	N(9)-Co(3)-N(10)	115.43(11)
Co(1)-N(3)	1.957(3)	N(11)-Co(3)-N(10)	109.14(12)
Co(1)-N(1)	1.966(3)	N(9)-Co(3)-N(12)	111.65(12)
Co(1)-N(2)	1.968(3)	N(11)-Co(3)-N(12)	109.53(12)
Co(1)-N(4)	1.970(3)	N(10)-Co(3)-N(12)	103.90(12)
S(1)-C(1)	1.626(3)	N(3)-Co(1)-N(1)	105.48(12)
S(9)-C(9)	1.625(4)	N(3)-Co(1)-N(2)	108.85(12)
S(4)-C(4)	1.628(4)	N(1)-Co(1)-N(2)	114.07(11)
S(11)-C(11)	1.624(3)	N(3)-Co(1)-N(4)	112.72(12)
S(12)-C(12)	1.630(4)	N(1)-Co(1)-N(4)	111.52(12)
S(3)-C(3)	1.618(3)	N(2)-Co(1)-N(4)	104.35(12)
S(5)-C(5)	1.623(4)	C(21)-N(15)-C(24)	109.9(2)
S(7)-C(7)	1.622(3)	C(23)-N(15)-C(24)	109.2(2)
S(2)-C(2)	1.621(4)	C(5)-N(5)-Co(2)	159.9(3)
S(10)-C(10)	1.622(3)	C(1)-N(1)-Co(1)	165.9(3)
S(8)-C(8)	1.614(3)	C(12)-N(12)-Co(3)	174.2(3)
S(6)-C(6)	1.616(4)	C(7)-N(7)-Co(2)	168.5(3)
N(14)-C(20)	1.487(5)	C(9)-N(9)-Co(3)	165.0(3)
N(14)-C(17)	1.491(4)	C(2)-N(2)-Co(1)	171.8(3)
N(14)-C(19)	1.491(4)	C(4)-N(4)-Co(1)	174.4(3)
N(14)-C(18)	1.492(4)	C(3)-N(3)-Co(1)	173.3(3)
N(5)-C(5)	1.156(4)	C(8)-N(8)-Co(2)	164.2(3)
N(1)-C(1)	1.169(4)	C(11)-N(11)-Co(3)	170.5(3)
N(13)-C(16)	1.493(4)	C(10)-N(10)-Co(3)	171.6(3)
N(13)-C(13)	1.496(4)	C(25)-N(16)-C(27)	109.5(3)
N(13)-C(15)	1.498(4)	C(6)-N(6)-Co(2)	168.1(3)
N(13)-C(14)	1.499(4)	N(7)-C(7)-S(7)	178.5(3)
N(12)-C(12)	1.165(4)	N(11)-C(11)-S(11)	179.1(3)
N(7)-C(7)	1.163(4)	N(4)-C(4)-S(4)	178.7(3)
N(9)-C(9)	1.161(4)	N(1)-C(1)-S(1)	178.5(3)
N(2)-C(2)	1.161(4)	N(8)-C(8)-S(8)	179.0(3)
N(4)-C(4)	1.167(4)	N(9)-C(9)-S(9)	179.0(3)
N(3)-C(3)	1.160(4)	N(3)-C(3)-S(3)	179.2(3)
N(8)-C(8)	1.158(4)	N(2)-C(2)-S(2)	179.6(3)
N(11)-C(11)	1.165(4)	N(5)-C(5)-S(5)	178.9(3)
N(10)-C(10)	1.151(4)	N(12)-C(12)-S(12)	178.9(3)
N(16)-C(25)	1.475(5)	N(6)-C(6)-S(6)	178.6(4)
N(6)-C(6)	1.150(4)	N(10)-C(10)-S(10)	179.4(3)

Figure S3: ORTEP drawing of compound **3**, $(C_4H_{12}N)_5[Co(NCS)_4][UO_2(NCS)_5]$.

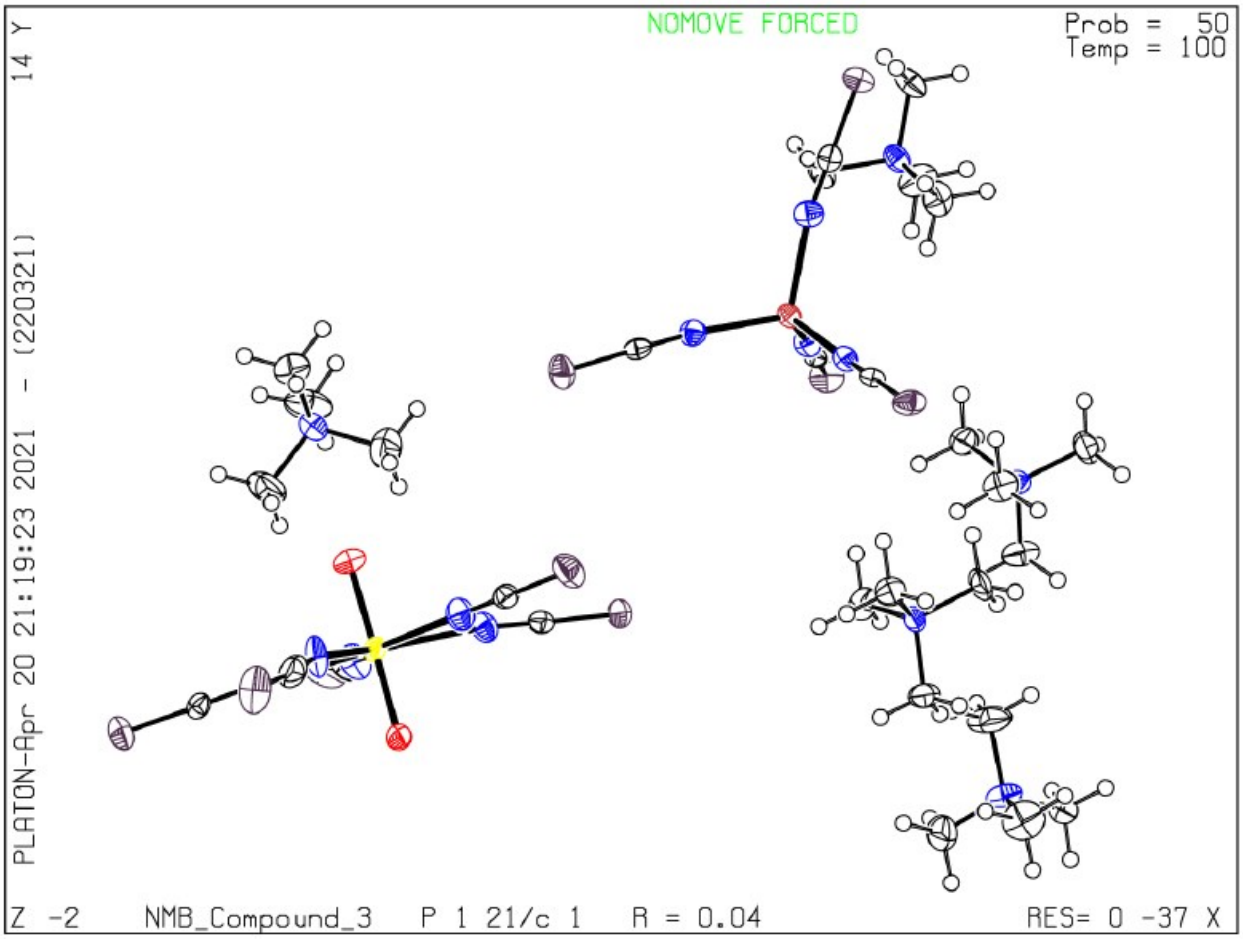

Table S4: Bond distances and angles for compound **3**, $(C_4H_{12}N)_5[Co(NCS)_4][UO_2(NCS)_5]$.

Atom 1-Atom 2	Bond Length (Å)	Atom 1-Atom 2-Atom 3	Bond Angle (°)	Atom 1-Atom 2-Atom 3	Bond Angle (°)
U(1)-O(1)	1.766(4)	O(1)-U(1)-O(2)	179.01(18)	C(12)-N(10)-C(11)	110.0(5)
U(1)-O(2)	1.774(4)	O(1)-U(1)-N(5)	90.95(18)	C(13)-N(10)-C(10)	109.8(5)
U(1)-N(5)	2.420(5)	O(2)-U(1)-N(5)	88.54(19)	C(12)-N(10)-C(10)	108.8(5)
U(1)-N(3)	2.435(5)	O(1)-U(1)-N(3)	92.14(17)	C(11)-N(10)-C(10)	108.4(5)
U(1)-N(4)	2.447(5)	O(2)-U(1)-N(3)	88.77(18)	C(7)-N(7)-Co(1)	169.4(4)
U(1)-N(2)	2.480(4)	N(5)-U(1)-N(3)	143.15(16)	C(16)-N(11)-C(17)	110.2(4)
U(1)-N(1)	2.487(5)	O(1)-U(1)-N(4)	88.29(16)	C(16)-N(11)-C(14)	108.9(4)
C(3)-N(3)	1.160(7)	O(2)-U(1)-N(4)	92.36(17)	C(17)-N(11)-C(14)	109.6(4)
C(3)-S(3)	1.617(6)	N(5)-U(1)-N(4)	72.23(16)	C(16)-N(11)-C(15)	109.2(4)
Co(1)-N(9)	1.948(5)	N(3)-U(1)-N(4)	71.17(16)	C(17)-N(11)-C(15)	109.3(5)
Co(1)-N(6)	1.953(5)	O(1)-U(1)-N(2)	90.05(17)	C(14)-N(11)-C(15)	109.6(5)
Co(1)-N(8)	1.957(4)	O(2)-U(1)-N(2)	89.85(18)	C(8)-N(8)-Co(1)	176.8(4)
Co(1)-N(7)	1.974(5)	N(5)-U(1)-N(2)	143.03(16)	C(6)-N(6)-Co(1)	172.9(4)
C(4)-N(4)	1.165(7)	N(3)-U(1)-N(2)	73.70(15)	C(9)-N(9)-Co(1)	168.6(4)
C(4)-S(4)	1.627(5)	N(4)-U(1)-N(2)	144.74(15)	C(18)-N(14)-C(20)	109.0(5)
C(5)-N(5)	1.104(7)	O(1)-U(1)-N(1)	89.26(16)	C(18)-N(14)-C(21)	109.8(5)
C(5)-S(5)	1.644(7)	O(2)-U(1)-N(1)	89.78(18)	C(20)-N(14)-C(21)	109.6(5)
S(8)-C(8)	1.618(5)	N(5)-U(1)-N(1)	71.09(16)	C(18)-N(14)-C(19)	109.3(4)
C(1)-N(1)	1.157(7)	N(3)-U(1)-N(1)	145.64(15)	C(20)-N(14)-C(19)	109.2(5)
C(1)-S(1)	1.626(5)	N(4)-U(1)-N(1)	143.18(16)	C(21)-N(14)-C(19)	109.8(5)
S(9)-C(9)	1.621(6)	N(2)-U(1)-N(1)	71.97(15)	N(6)-C(6)-S(6)	179.1(5)
S(6)-C(6)	1.616(5)	N(3)-C(3)-S(3)	179.2(6)	N(9)-C(9)-S(9)	178.9(5)
S(7)-C(7)	1.632(6)	N(9)-Co(1)-N(6)	106.94(18)	N(8)-C(8)-S(8)	179.5(5)
N(12)-C(23)	1.484(7)	N(9)-Co(1)-N(8)	117.38(19)	N(7)-C(7)-S(7)	179.6(5)
N(12)-C(24)	1.488(7)	N(6)-Co(1)-N(8)	110.35(19)	C(2)-N(2)-U(1)	168.0(5)
N(12)-C(22)	1.493(7)	N(9)-Co(1)-N(7)	105.55(19)	N(2)-C(2)-S(2)	176.7(6)
N(12)-C(25)	1.506(7)	N(6)-Co(1)-N(7)	109.60(19)		
N(13)-C(29)	1.491(7)	N(8)-Co(1)-N(7)	106.77(18)		
N(13)-C(28)	1.492(7)	N(4)-C(4)-S(4)	178.7(5)		
N(13)-C(26)	1.493(7)	C(3)-N(3)-U(1)	172.7(4)		
N(13)-C(27)	1.494(7)	N(5)-C(5)-S(5)	177.6(7)		
N(10)-C(13)	1.472(8)	C(4)-N(4)-U(1)	170.1(4)		
N(10)-C(12)	1.495(8)	N(1)-C(1)-S(1)	178.6(5)		
N(10)-C(11)	1.496(8)	C(5)-N(5)-U(1)	176.8(5)		
N(10)-C(10)	1.505(7)	C(1)-N(1)-U(1)	174.2(4)		
N(7)-C(7)	1.162(7)	C(23)-N(12)-C(24)	109.8(5)		
N(11)-C(16)	1.497(7)	C(23)-N(12)-C(22)	109.3(4)		
N(11)-C(17)	1.498(7)	C(24)-N(12)-C(22)	109.5(5)		
N(11)-C(14)	1.501(7)	C(23)-N(12)-C(25)	109.6(4)		
N(11)-C(15)	1.502(7)	C(24)-N(12)-C(25)	109.6(4)		
N(8)-C(8)	1.159(6)	C(22)-N(12)-C(25)	109.1(5)		
N(6)-C(6)	1.164(7)	C(29)-N(13)-C(28)	109.2(4)		
N(9)-C(9)	1.168(7)	C(29)-N(13)-C(26)	110.8(4)		
N(14)-C(18)	1.475(8)	C(28)-N(13)-C(26)	109.8(4)		
N(14)-C(20)	1.489(8)	C(29)-N(13)-C(27)	109.6(4)		
N(14)-C(21)	1.494(7)	C(28)-N(13)-C(27)	110.4(4)		
N(14)-C(19)	1.517(7)	C(26)-N(13)-C(27)	107.0(5)		
S(2)-C(2)	1.651(8)	C(13)-N(10)-C(12)	110.3(5)		
N(2)-C(2)	1.105(8)	C(13)-N(10)-C(11)	109.5(5)		

Synthetic Procedure for compounds 4-7: Compounds **4-7** were synthesized during a comprehensive effort to prepare other potential heterometallic UO_2^{2+}/Co^{2+} phases. Similar to TMA^+, cations (tetraethylammonium (TEA^+) and cesium (Cs^+)) were selected due to their inability to participate in meaningful non-covalent interactions, as assembly via electrostatic attraction was expected. Pyridine (Py^+), however, was chosen to determine the role of hydrogen bonding on assembly in these materials. These synthetic attempts sought to pair the $[UO_2(NCS)_5]^{3-}$ and/or $[Co(NCS)_4]^{2-}$, with TMA^+, TEA^+, Cs^+, and Py^+ present to provide charge balance. In the case of TEA^+, Cs^+, and Py^+, no heterometallics phases were observed. We also prepared a polymorph of **1**, which appeared as a secondary product during synthesis. Compounds **4-7** represent the importance of strict cation and/or synthesis parameters for **1-3**, as slight changes to reaction conditions or cation identity led to structural variation and prevented the formation of heterometallic phases.

*Homometallic Co phase: Compound **4*** $Cs_3[Co(NCS)_4](NCS)$

Cobalt chloride hexahydrate (0.025g, 0.105 mmol) and 6 equivalents of KSCN (0.0613 g, 0.631 mmol) were added to 5 mL of H_2O in a 20 mL glass scintillation vial. To this solution, 3 molar equivalents of Cs^+ were added. All reactions were left to evaporate to dryness at room temperature, with crystals forming rapidly over the course of several hours.

*Homometallic U-phases: Compound **5-7***

Caution! Although the uranium source used (uranyl acetate dihydrate $[UO_2(CH_3COO)_2]\cdot 2H_2O$) contains depleted uranium, precautions for handling radioactive materials should be followed.

Uranyl acetate dihydrate (0.025 g, 0.059 mmol) and 6 molar equivalents of potassium thiocyanate (0.0344 g, 0.354 mmol) were added to 5 mL of water in a 20 mL glass scintillation vial. To the resultant clear, yellow solution, 4 molar equivalents of the desired cation (tetramethylammonium (TMA^+), tetraethylammonium (TEA^+), cesium (Cs^+), or pyridinium (Py^+)) were added. The pH was adjusted from approximately 6.5 to 4 using concentrated HCl, to allow for protonation of the organic if necessary and serve to restrict uranyl speciation. Solutions were left to evaporate to dryness in the fume hood over the course of several days. These phases may also be prepared hydrothermally at 90°C for 72 hours in a Teflon-lined acid digestion vessel. Performing the hydrothermal syntheses at temperatures above 100°C or at a pH below 3, however results in -NCS ligand degradation.

Table S5: Crystallography table for compounds **4-7**

	4	**5**	**6**
Chemical Formula	$Cs_9[Co(NCS)_4]_4(NCS)$	$(C_8H_{20}N)_2[UO_2(NCS)_4(H2O)]\cdot H_2O$	$(C_5H_6N)_3[UO_2(NCS)_5]\cdot H_2O,C_5H_5N$
Formula Weight (g/mol)	2419.3	798.9	818.8
Crystal System	Monoclinic	Orthorhombic	Monoclinic
Space Group	$P2_1/c$	$Pna2_1$	$P2_1/c$
a (Å)	25.482(1)	30.443(3)	16.616(1)
b (Å)	11.912(1)	7.848(1)	10.747(1)
c (Å)	21.147(1)	13.503(1)	16.179(1)
α (°)	90	90	90
β (°)	114.254(1)	90	91.766(1)
γ (°)	90	90	90
V (Å^3)	5852.3(3)	3226.0(6)	2887.7(2)
Z	4	4	4
T (K)	100(2)	100(2)	100(2)
λ (Mo Kα)	0.71073	0.71073	0.71073
μ (mm^{-1})	7.275	5.323	6.020
R_{int}	0.0322	0.0660	0.0410
R_1	0.0211	0.0308	0.0167
wR2	0.0478	0.0608	0.0358
	7		
Chemical Formula	$(C_4H_{12}N)_6[UO_2(NCS)_5]_2\cdot H_2O$		
Formula Weight	782.9		
Crystal System	Orthorhombic		
Space Group	Pbca		
a (Å)	13.921(1)		
b (Å)	13.221(1)		
c (Å)	34.149(2)		
α (°)	90		
β (°)	90		
γ (°)	90		
V (Å^3)	6285.1(6)		
Z	8		
T (K)	100(2)		
λ (Mo Kα)	0.71073		
μ (mm^{-1})	5.524		
R_{int}	0.0574		
R_1	0.0409		
wR2	0.0774		

Figure S4: ORTEP drawing of compound **4**, $Cs_9[Co(NCS)_4]_4(NCS)$.

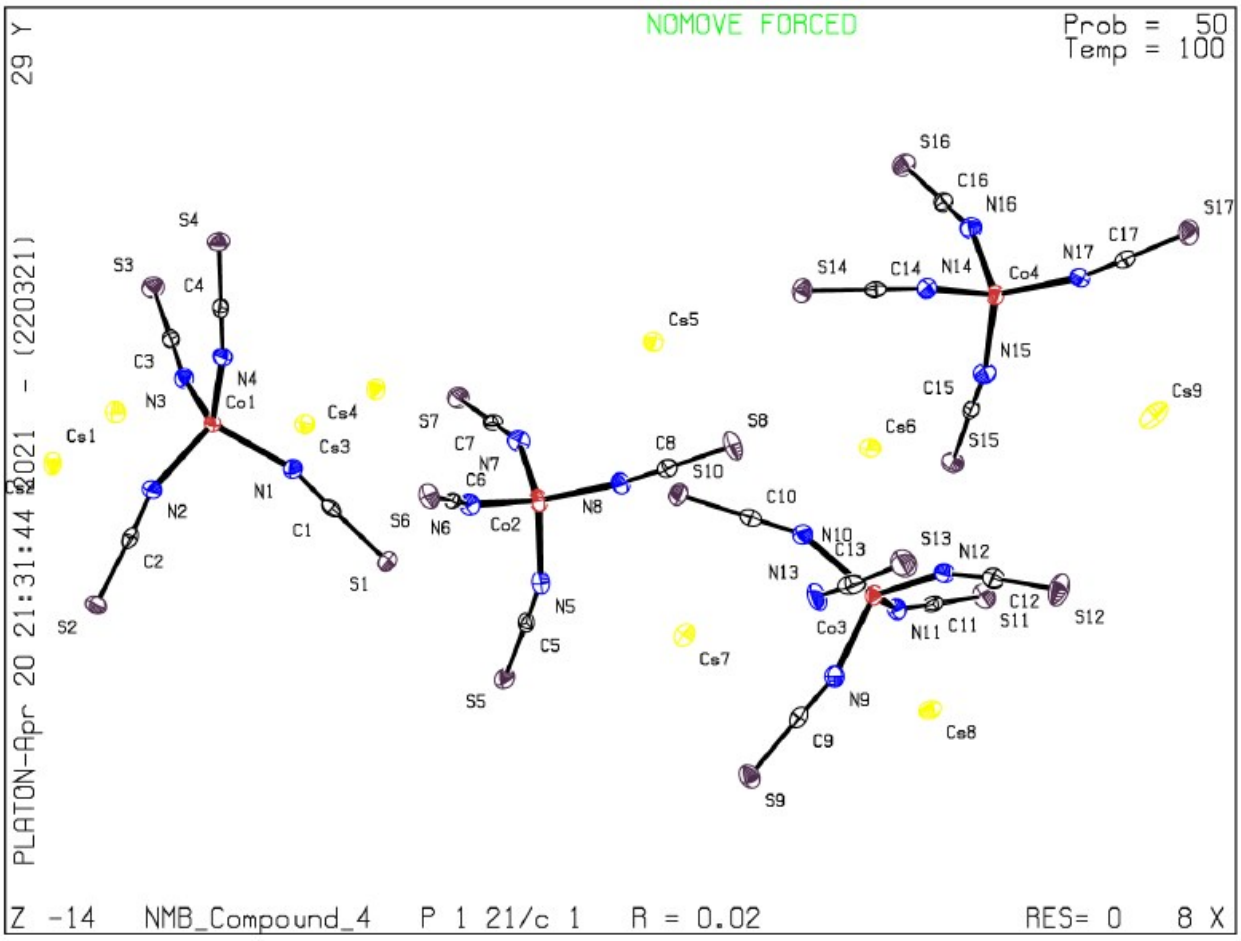

Table S6: Bond distances and angles for compound **4**, $Cs_9[Co(NCS)_4]_4(NCS)$

Atom 1-Atom 2	Bond Length (Å)	Atom 1-Atom 2-Atom 3	Bond Angle (°)
Co(1)-N(4)	1.965(3)	N(4)-Co(1)-N(3)	104.85(13)
Co(1)-N(3)	1.965(3)	N(3)-Co(1)-N(1)	110.17(13)
Co(1)-N(1)	1.966(3)	N(4)-Co(1)-N(2)	112.69(13)
Co(1)-N(2)	1.968(3)	N(3)-Co(1)-N(2)	112.67(13)
Co(2)-N(8)	1.947(3)	N(1)-Co(1)-N(2)	112.19(13)
Co(2)-N(6)	1.959(3)	N(8)-Co(2)-N(6)	104.46(13)
Co(2)-N(7)	1.981(3)	N(8)-Co(2)-N(7)	113.38(13)
Co(2)-N(5)	1.988(3)	N(6)-Co(2)-N(7)	111.99(13)
Co(4)-N(17)	1.953(3)	N(8)-Co(2)-N(5)	111.39(13)
Co(4)-N(15)	1.956(3)	N(7)-Co(2)-N(5)	108.36(13)
Co(4)-N(14)	1.983(3)	N(17)-Co(4)-N(15)	100.73(13)
Co(4)-N(16)	1.988(3)	N(17)-Co(4)-N(14)	116.58(13)
Co(3)-N(12)	1.945(3)	N(15)-Co(4)-N(14)	114.71(13)
Co(3)-N(10)	1.977(3)	N(12)-Co(3)-N(10)	101.83(13)
Co(3)-N(11)	1.978(3)	N(12)-Co(3)-N(11)	113.03(13)
Co(3)-N(9)	1.986(3)	N(10)-Co(3)-N(11)	114.84(13)
S(1)-C(1)	1.627(4)	N(12)-Co(3)-N(9)	109.61(13)
S(4)-C(4)	1.624(4)	N(10)-Co(3)-N(9)	110.56(13)
S(16)-C(16)	1.632(4)	N(11)-Co(3)-N(9)	103.05(13)
S(2)-C(2)	1.629(4)	C(7)-N(7)-Co(2)	104.79(13)
S(14)-C(14)	1.625(4)	C(8)-N(8)-Co(2)	157.0(3)
S(15)-C(15)	1.631(4)	C(17)-N(17)-Co(4)	173.9(3)
S(7)-C(7)	1.625(4)	N(3)-C(3)-S(3)	167.5(3)
S(3)-C(3)	1.622(4)	C(16)-N(16)-Co(4)	176.7(4)
S(10)-C(10)	1.623(4)	C(4)-N(4)-Co(1)	158.5(3)
S(6)-C(6)	1.610(4)	C(5)-N(5)-Co(2)	162.4(3)
S(9)-C(9)	1.622(4)	N(4)-C(4)-S(4)	160.1(3)
S(5)-C(5)	1.618(4)	N(11)-C(11)-S(11)	177.7(4)
S(11)-C(11)	1.620(4)	C(3)-N(3)-Co(1)	178.7(4)
S(8)-C(8)	1.624(4)	C(9)-N(9)-Co(3)	163.6(3)
S(12)-C(12)	1.615(4)	C(15)-N(15)-Co(4)	117.22(9)
S(17)-C(17)	1.621(4)	C(10)-N(10)-Co(3)	114.23(9)
S(13)-C(13)	1.652(6)	N(6)-C(6)-S(6)	156.8(3)
N(12)-C(12)	1.173(5)	C(6)-N(6)-Co(2)	179.4(4)
N(7)-C(7)	1.163(5)	C(11)-N(11)-Co(3)	149.0(3)
N(8)-C(8)	1.161(5)	N(15)-C(15)-S(15)	150.3(3)
N(17)-C(17)	1.172(5)	C(14)-N(14)-Co(4)	178.3(4)
C(3)-N(3)	1.171(5)	C(2)-N(2)-Co(1)	157.1(3)
N(16)-C(16)	1.166(5)	N(9)-C(9)-S(9)	162.9(3)
N(4)-C(4)	1.168(5)	N(12)-C(12)-S(12)	177.8(4)
N(5)-C(5)	1.164(5)	N(16)-C(16)-S(16)	175.7(4)
C(11)-N(11)	1.173(5)	N(2)-C(2)-S(2)	177.4(4)
N(9)-C(9)	1.162(5)	N(10)-C(10)-S(10)	177.8(3)
N(15)-C(15)	1.159(5)	N(13)-C(13)-S(13)	179.9(4)
N(10)-C(10)	1.170(5)	N(14)-C(14)-S(14)	178.3(4)
C(6)-N(6)	1.183(5)	N(8)-C(8)-S(8)	178.2(3)
N(14)-C(14)	1.167(5)	N(1)-C(1)-S(1)	178.2(4)
N(2)-C(2)	1.165(5)	N(5)-C(5)-S(5)	178.0(3)
C(13)-N(13)	1.097(6)	N(17)-C(17)-S(17)	178.6(3)
N(1)-C(1)	1.168(5)	N(7)-C(7)-S(7)	177.7(4)

Figure S5: ORTEP drawing of compound **5**, $(C_8H_{20}N)_2[UO_2(NCS)_4(H_2O)]\cdot H_2O$.

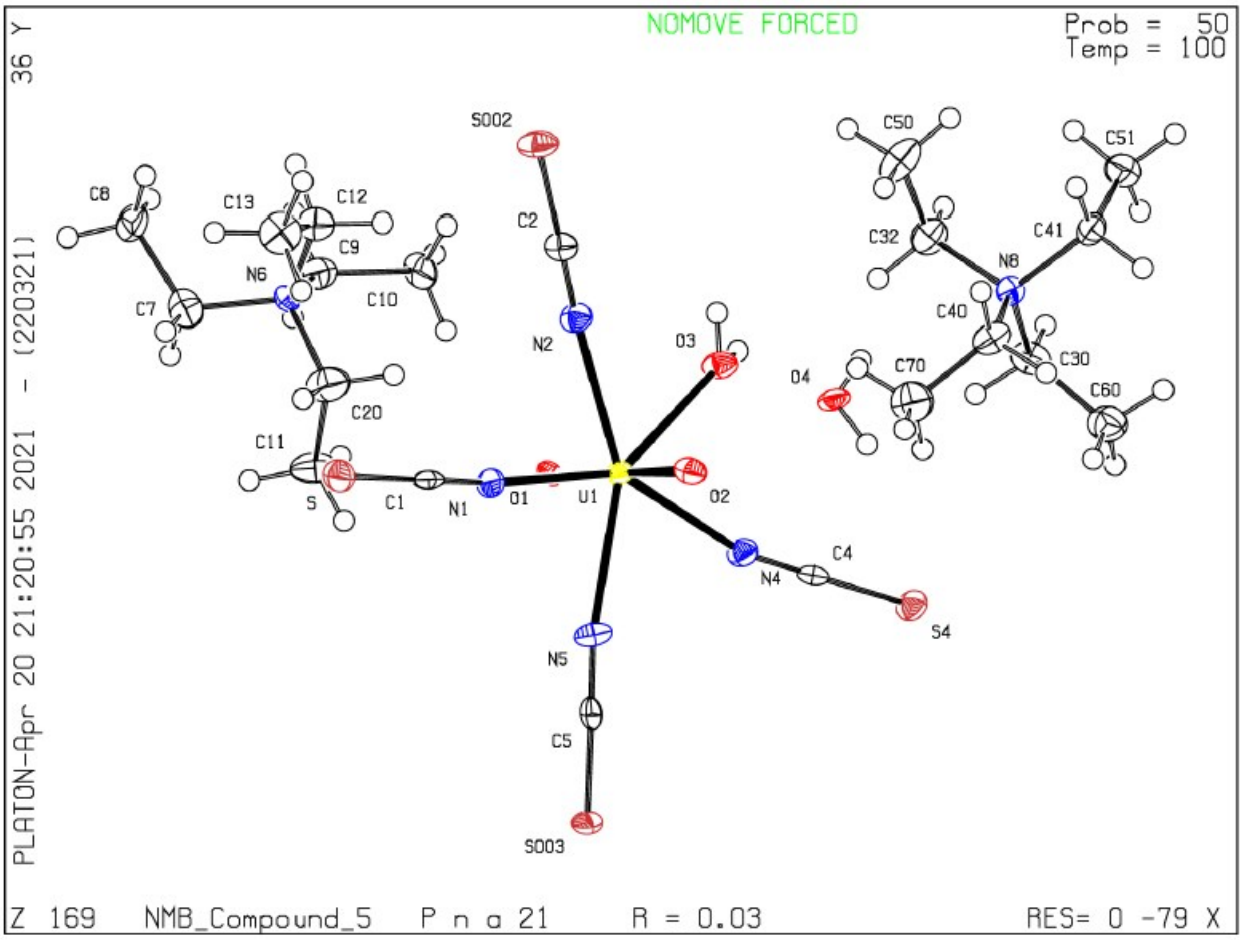

Table S7: Bond distances and angles for compound **5**, $(C_8H_{20}N)_2[UO_2(NCS)_4(H_2O)]\cdot H_2O$

Atom 1-Atom 2	Bond Length (Å)	Atom 1-Atom 2-Atom 3	Bond Angle (°)
U(1)-O(2)	1.760(5)	O(2)-U(1)-O(1)	179.0(3)
U(1)-O(1)	1.772(4)	O(2)-U(1)-N(1)	88.8(2)
U(1)-N(1)	2.417(6)	O(1)-U(1)-N(1)	92.1(2)
U(1)-N(2)	2.426(10)	O(2)-U(1)-N(2)	89.3(4)
U(1)-N(5)	2.437(9)	O(1)-U(1)-N(2)	90.4(3)
U(1)-N(4)	2.448(9)	N(1)-U(1)-N(2)	74.4(3)
U(1)-O(3)	2.495(7)	O(2)-U(1)-N(5)	92.0(4)
S(002)-C(2)	1.636(12)	O(1)-U(1)-N(5)	88.8(3)
S(003)-C(5)	1.625(12)	N(1)-U(1)-N(5)	75.7(3)
S-C(1)	1.629(9)	N(2)-U(1)-N(5)	150.0(3)
N(2)-C(2)	1.150(14)	O(2)-U(1)-N(4)	86.6(3)
O(3)-H(3A)	0.80(3)	O(1)-U(1)-N(4)	93.0(3)
O(3)-H(3B)	0.80(3)	N(1)-U(1)-N(4)	147.1(3)
N(1)-C(1)	1.153(10)	N(2)-U(1)-N(4)	138.0(3)
C(10)-C(9)	1.526(13)	N(5)-U(1)-N(4)	72.0(3)
C(5)-N(5)	1.169(13)	O(2)-U(1)-O(3)	91.9(3)
N(4)-C(4)	1.162(11)	O(1)-U(1)-O(3)	87.1(3)
C(9)-N(6)	1.506(11)	N(1)-U(1)-O(3)	144.0(3)
C(13)-C(12)	1.524(12)	N(2)-U(1)-O(3)	69.6(3)
C(7)-N(6)	1.508(11)	N(5)-U(1)-O(3)	140.2(3)
C(7)-C(8)	1.518(12)	N(4)-U(1)-O(3)	68.8(2)
N(6)-C(20)	1.481(11)	C(2)-N(2)-U(1)	169.9(9)
N(6)-C(12)	1.512(10)	C(1)-N(1)-U(1)	174.0(7)
C(11)-C(20)	1.547(14)	N(5)-C(5)-S(003)	178.7(10)
C(4)-S(4)	1.635(9)	C(4)-N(4)-U(1)	163.6(7)
O(4)-H(4A)	0.83(3)	N(2)-C(2)-S(002)	178.8(11)
O(4)-H(4B)	0.83(3)	N(6)-C(9)-C(10)	115.3(7)
C(60)-C(30)	1.515(17)	N(6)-C(7)-C(8)	116.2(7)
C(30)-N(8)	1.503(10)	N(1)-C(1)-S	178.8(8)
C(32)-N(8)	1.516(10)	C(20)-N(6)-C(9)	111.7(7)
C(32)-C(50)	1.527(12)	C(20)-N(6)-C(7)	109.3(7)
N(8)-C(40)	1.518(10)	C(9)-N(6)-C(7)	108.0(6)
N(8)-C(41)	1.522(10)	C(20)-N(6)-C(12)	107.9(7)
C(40)-C(70)	1.510(12)	C(9)-N(6)-C(12)	108.4(6)
C(41)-C(51)	1.531(14)	C(7)-N(6)-C(12)	111.5(6)
		N(6)-C(12)-C(13)	115.6(7)
		C(5)-N(5)-U(1)	165.6(8)
		N(4)-C(4)-S(4)	178.1(8)
		N(6)-C(20)-C(11)	116.7(8)
		N(8)-C(30)-C(60)	115.9(8)
		N(8)-C(32)-C(50)	114.2(8)
		C(30)-N(8)-C(32)	107.0(6)
		C(30)-N(8)-C(40)	110.7(6)
		C(32)-N(8)-C(40)	111.2(6)
		C(30)-N(8)-C(41)	111.2(6)
		C(32)-N(8)-C(41)	111.4(6)
		C(40)-N(8)-C(41)	105.4(6)
		C(70)-C(40)-N(8)	114.6(7)
		N(8)-C(41)-C(51)	115.7(8)

Figure S6: ORTEP drawing of compound **6**, $(C_5H_6N)_3[UO_2(NCS)_5]\cdot H_2O,C_5H_5N$

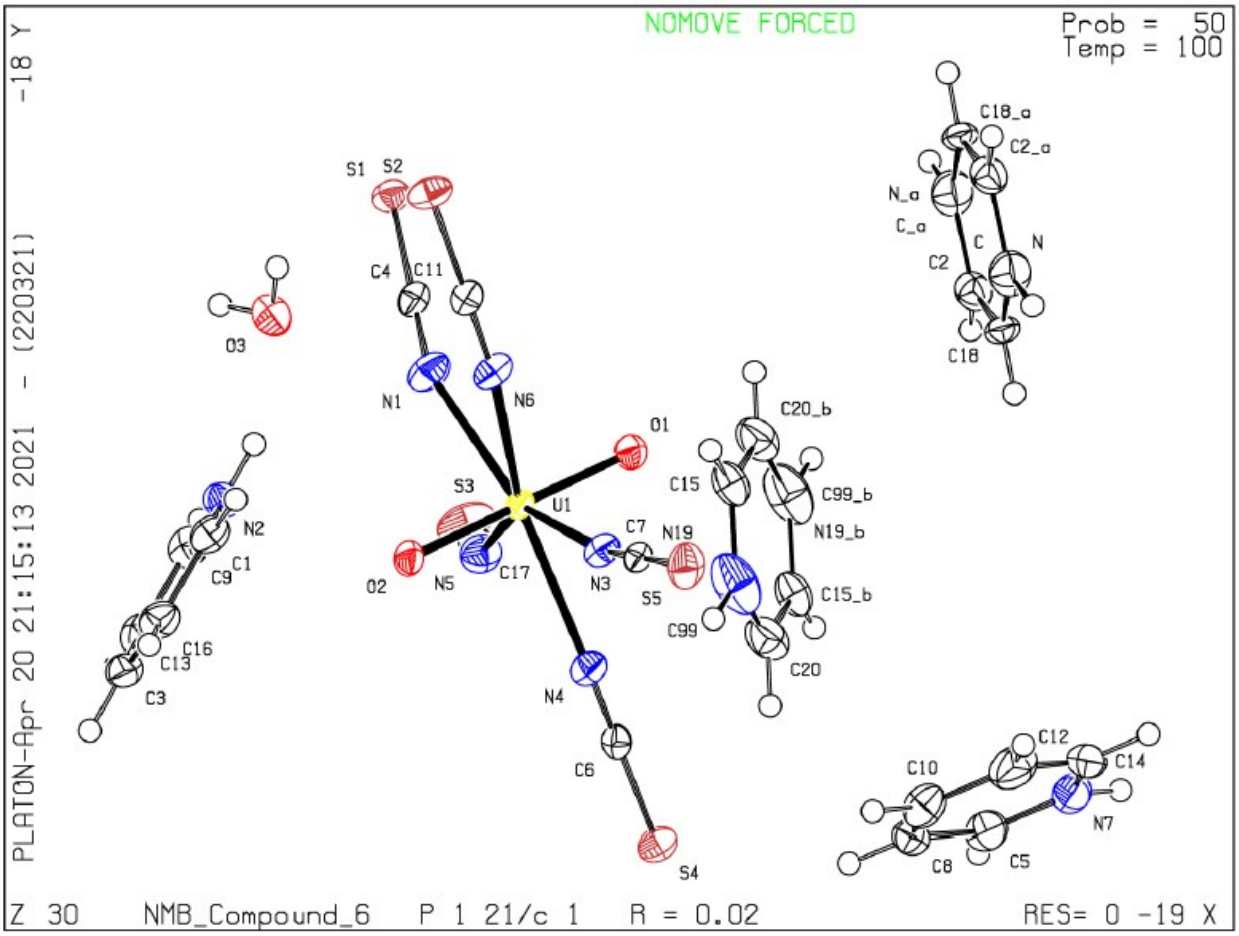

Table S8: Bond distances and angles for compound **6,** $(C_5H_6N)_3[UO_2(NCS)_5]\cdot H_2O,C_5H_5N$

Atom 1-Atom 2	Bond Length (Å)	Atom 1-Atom 2-Atom 3	Bond Angle (°)
U(1)-O(1)	1.7692(16)	O(2)-U(1)-O(1)	179.7(2)
U(1)-O(2)	1.7712(16)	O(2)-U(1)-N(4)	92.3(2)
U(1)-N(3)	2.443(2)	O(1)-U(1)-N(4)	87.7(2)
U(1)-N(1)	2.446(2)	O(2)-U(1)-N(1)	92.08(19)
U(1)-N(5)	2.447(2)	O(1)-U(1)-N(1)	87.81(18)
U(1)-N(4)	2.448(2)	N(4)-U(1)-N(1)	144.12(18)
U(1)-N(6)	2.463(2)	O(2)-U(1)-N(5)	87.25(19)
N(1)-C(4)	1.155(3)	O(1)-U(1)-N(5)	92.48(19)
S(2)-C(11)	1.640(2)	N(4)-U(1)-N(5)	71.84(18)
N(6)-C(11)	1.156(3)	N(1)-U(1)-N(5)	72.82(17)
S(1)-C(4)	1.635(3)	O(2)-U(1)-N(3)	90.67(18)
N(3)-C(7)	1.162(3)	O(1)-U(1)-N(3)	89.56(18)
S(4)-C(6)	1.623(2)	N(4)-U(1)-N(3)	72.34(18)
N(4)-C(6)	1.162(3)	N(1)-U(1)-N(3)	143.18(17)
S(5)-C(7)	1.628(3)	N(5)-U(1)-N(3)	144.00(18)
N(5)-C(17)	1.141(3)	O(2)-U(1)-N(2)	90.67(19)
S(3)-C(17)	1.634(3)	O(1)-U(1)-N(2)	89.53(18)
C(16)-C(1)	1.366(4)	N(4)-U(1)-N(2)	143.94(18)
C(16)-C(3)	1.386(4)	N(1)-U(1)-N(2)	71.56(17)
N(2)-C(9)	1.331(3)	N(5)-U(1)-N(2)	144.22(18)
N(2)-C(1)	1.345(3)	N(3)-U(1)-N(2)	71.69(17)
C(3)-C(13)	1.372(4)	C(5)-N(5)-U(1)	171.4(5)
C(9)-C(13)	1.371(4)	C(3)-N(3)-U(1)	173.4(5)
O(3)-H(3A)	0.94(4)	C(8)-N(6)-C(6)	109.9(6)
O(3)-H(3B)	0.86(4)	C(8)-N(6)-C(9)	109.7(5)
		C(6)-N(6)-C(9)	108.7(5)
		C(8)-N(6)-C(7)	109.7(5)
		C(6)-N(6)-C(7)	109.0(6)
		C(9)-N(6)-C(7)	109.9(6)
		C(2)-N(2)-U(1)	172.1(5)
		C(4)-N(4)-U(1)	164.3(5)
		N(2)-C(2)-S(2)	179.5(6)
		N(4)-C(4)-S(4)	178.1(6)
		C(10)-N(7)-C(13)	110.0(5)
		C(10)-N(7)-C(12)	110.2(5)
		C(13)-N(7)-C(12)	109.6(5)
		C(10)-N(7)-C(11)	109.1(5)
		C(13)-N(7)-C(11)	109.6(6)
		C(12)-N(7)-C(11)	108.3(5)
		C(17)-N(8)-C(14)	109.8(5)
		C(17)-N(8)-C(15)	109.9(5)
		C(14)-N(8)-C(15)	109.4(5)
		C(17)-N(8)-C(16)	109.0(5)
		C(14)-N(8)-C(16)	109.4(5)
		C(15)-N(8)-C(16)	109.3(5)
		N(1)-C(1)-S(1)	178.8(6)
		N(3)-C(3)-S(3)	178.5(6)
		N(5)-C(5)-S(5)	178.0(6)
		C(1)-N(1)-U(1)	173.6(5)

Figure S7: ORTEP drawing of compound **7**, $(C_4H_{12}N)_3[UO_2(NCS)_5]$

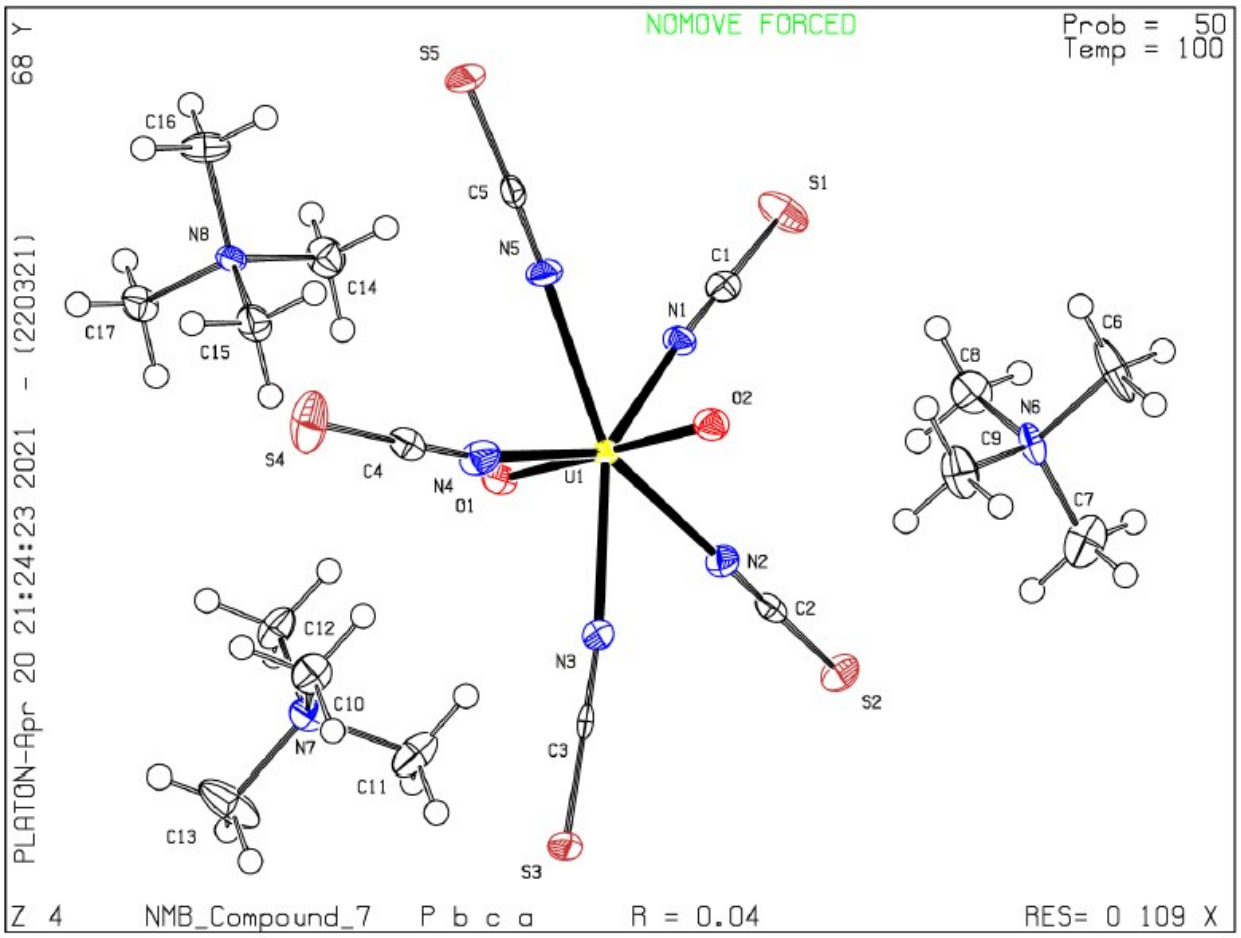

Table S9: Bond distances and angles for compound **7**, $(C_4H_{12}N)_3[UO_2(NCS)_5]$

Atom 1-Atom 2	Bond Length (Å)	Atom 1-Atom 2-Atom 3	Bond Angle (°)
U(1)-O(2)	1.764(4)	O(2)-U(1)-O(1)	179.7(2)
U(1)-O(1)	1.776(4)	O(2)-U(1)-N(4)	92.3(2)
U(1)-N(4)	2.427(6)	O(1)-U(1)-N(4)	87.7(2)
U(1)-N(1)	2.430(5)	O(2)-U(1)-N(1)	92.08(19)
U(1)-N(5)	2.437(5)	O(1)-U(1)-N(1)	87.81(18)
U(1)-N(3)	2.453(5)	N(4)-U(1)-N(1)	144.12(18)
U(1)-N(2)	2.461(5)	O(2)-U(1)-N(5)	87.25(19)
S(2)-C(2)	1.636(6)	O(1)-U(1)-N(5)	92.48(19)
S(3)-C(3)	1.631(6)	N(4)-U(1)-N(5)	71.84(18)
S(1)-C(1)	1.628(7)	N(1)-U(1)-N(5)	72.82(17)
S(5)-C(5)	1.632(6)	O(2)-U(1)-N(3)	90.67(18)
S(4)-C(4)	1.612(7)	O(1)-U(1)-N(3)	89.56(18)
N(5)-C(5)	1.155(8)	N(4)-U(1)-N(3)	72.34(18)
N(3)-C(3)	1.160(8)	N(1)-U(1)-N(3)	143.18(17)
N(6)-C(8)	1.489(8)	N(5)-U(1)-N(3)	144.00(18)
N(6)-C(6)	1.489(8)	O(2)-U(1)-N(2)	90.67(19)
N(6)-C(9)	1.490(8)	O(1)-U(1)-N(2)	89.53(18)
N(6)-C(7)	1.500(9)	N(4)-U(1)-N(2)	143.94(18)
N(2)-C(2)	1.163(8)	N(1)-U(1)-N(2)	71.56(17)
N(4)-C(4)	1.162(8)	N(5)-U(1)-N(2)	144.22(18)
N(7)-C(10)	1.488(8)	N(3)-U(1)-N(2)	71.69(17)
N(7)-C(13)	1.490(8)	C(5)-N(5)-U(1)	171.4(5)
N(7)-C(12)	1.491(8)	C(3)-N(3)-U(1)	173.4(5)
N(7)-C(11)	1.507(8)	C(8)-N(6)-C(6)	109.9(6)
N(8)-C(17)	1.489(7)	C(8)-N(6)-C(9)	109.7(5)
N(8)-C(14)	1.489(8)	C(6)-N(6)-C(9)	108.7(5)
N(8)-C(15)	1.491(8)	C(8)-N(6)-C(7)	109.7(5)
N(8)-C(16)	1.501(8)	C(6)-N(6)-C(7)	109.0(6)
C(1)-N(1)	1.157(8)	C(9)-N(6)-C(7)	109.9(6)
		C(2)-N(2)-U(1)	172.1(5)
		C(4)-N(4)-U(1)	164.3(5)
		N(2)-C(2)-S(2)	179.5(6)
		N(4)-C(4)-S(4)	178.1(6)
		C(10)-N(7)-C(13)	110.0(5)
		C(10)-N(7)-C(12)	110.2(5)
		C(13)-N(7)-C(12)	109.6(5)
		C(10)-N(7)-C(11)	109.1(5)
		C(13)-N(7)-C(11)	109.6(6)
		C(12)-N(7)-C(11)	108.3(5)
		C(17)-N(8)-C(14)	109.8(5)
		C(17)-N(8)-C(15)	109.9(5)
		C(14)-N(8)-C(15)	109.4(5)
		C(17)-N(8)-C(16)	109.0(5)
		C(14)-N(8)-C(16)	109.4(5)
		C(15)-N(8)-C(16)	109.3(5)
		N(1)-C(1)-S(1)	178.8(6)
		N(3)-C(3)-S(3)	178.5(6)
		N(5)-C(5)-S(5)	178.0(6)
		C(1)-N(1)-U(1)	173.6(5)

Figure S8: The PXRD pattern of the bulk product from the synthesis of **1** in black, which also produces **7**. The calculated pattern from 100(2) K SC-XRD data of **1** is overlaid in blue, and **7** in green. The PXRD pattern of the metathesis product of KSCN and $C_4H_{12}NCl$, which forms as a secondary product in the unoptimized synthesis of **1**, is shown in red.

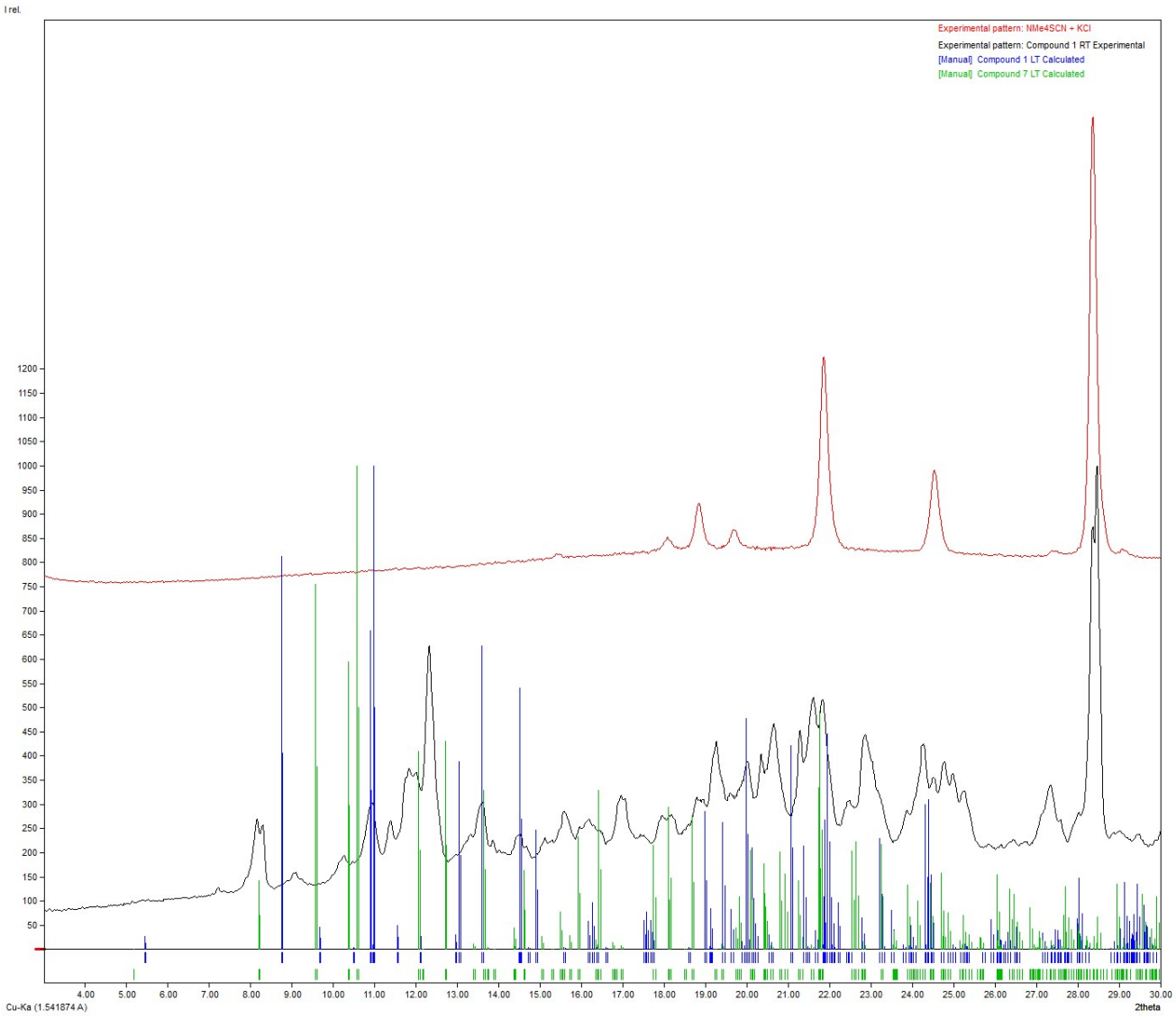

Figure S9: The PXRD pattern of the bulk product from the synthesis of **2** in black. The calculated pattern from 100(2) K SC-XRD data of **2** is overlaid in blue. The PXRD pattern of the metathesis product of KSCN and $C_4H_{12}NCl$, which forms as a secondary product in the unoptimized synthesis of **2**, is shown in red.

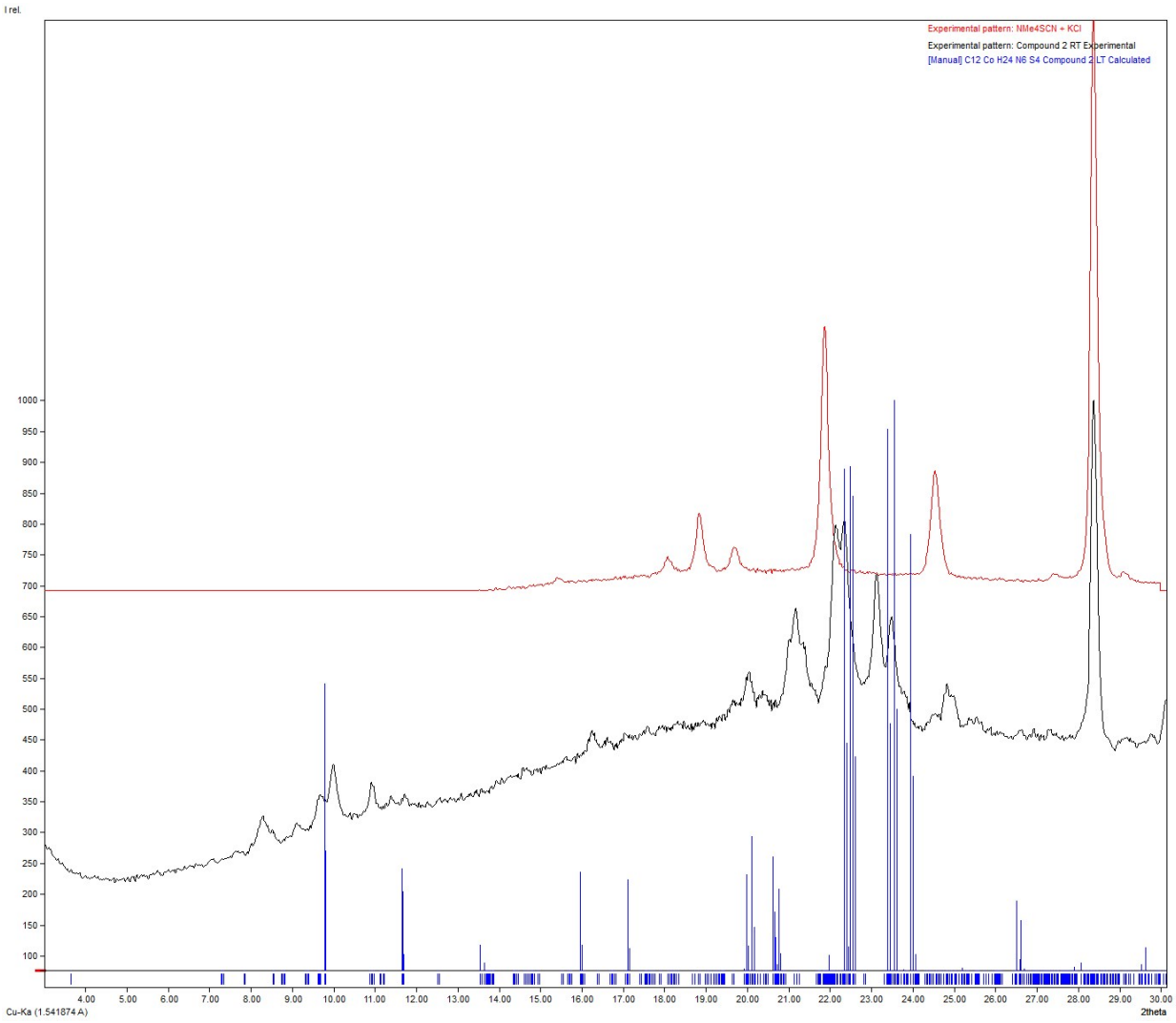

Figure S10: The PXRD pattern of the bulk product from the synthesis of **3** in black. The calculated pattern from 100(2) K SC-XRD data of **3** is overlaid in blue. The PXRD pattern of the metathesis product of KSCN and $C_4H_{12}NCl$, which forms as a secondary product in the unoptimized synthesis of **3**, is shown in red.

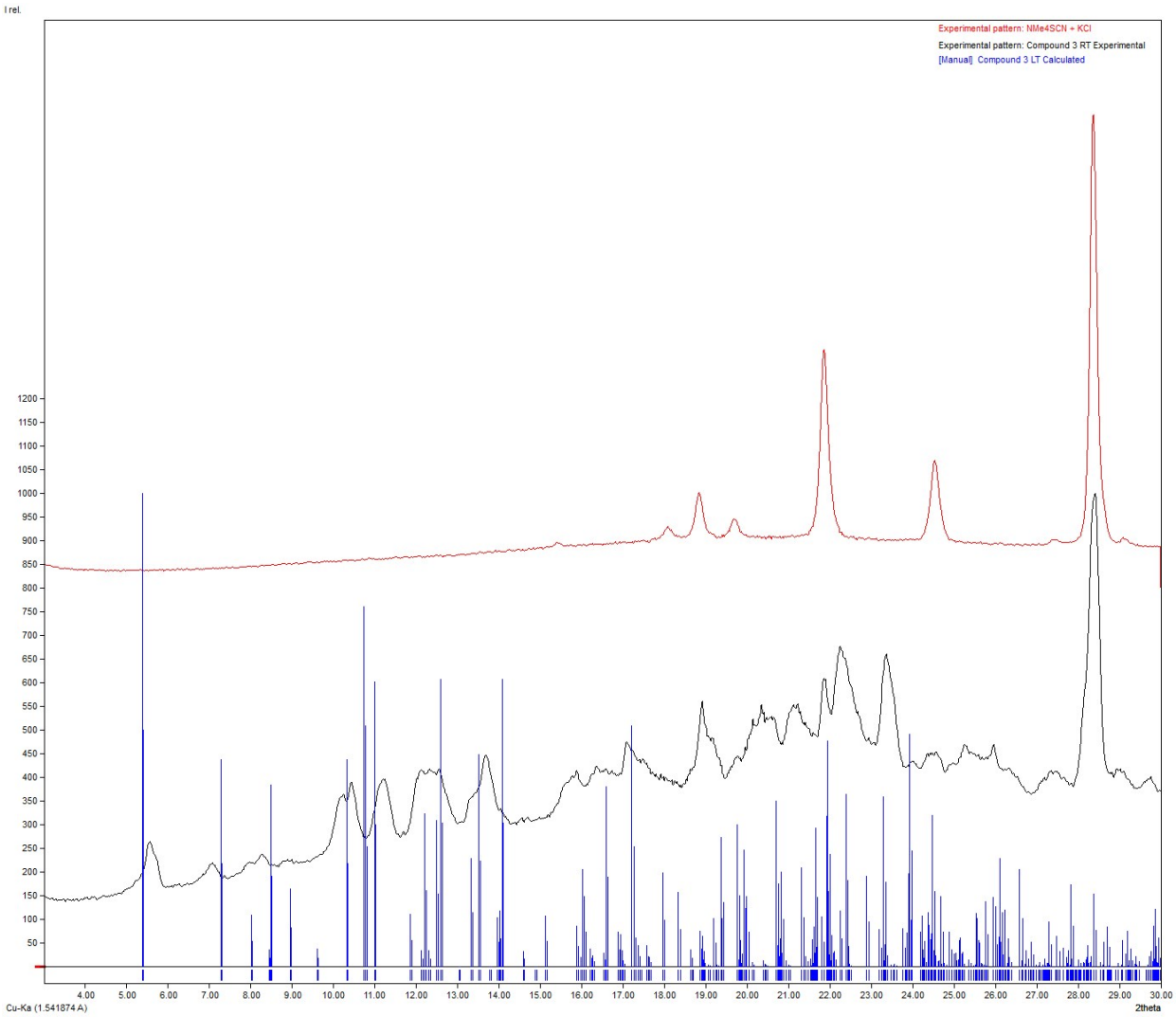

Figure S11: The PXRD pattern of the bulk product from the synthesis of **4** in black. The calculated pattern from 100(2) K SC-XRD data of **4** is overlaid in blue. The pattern of KCl is shown in green, which forms as a metathesis byproduct of excess KSCN and CsCl.

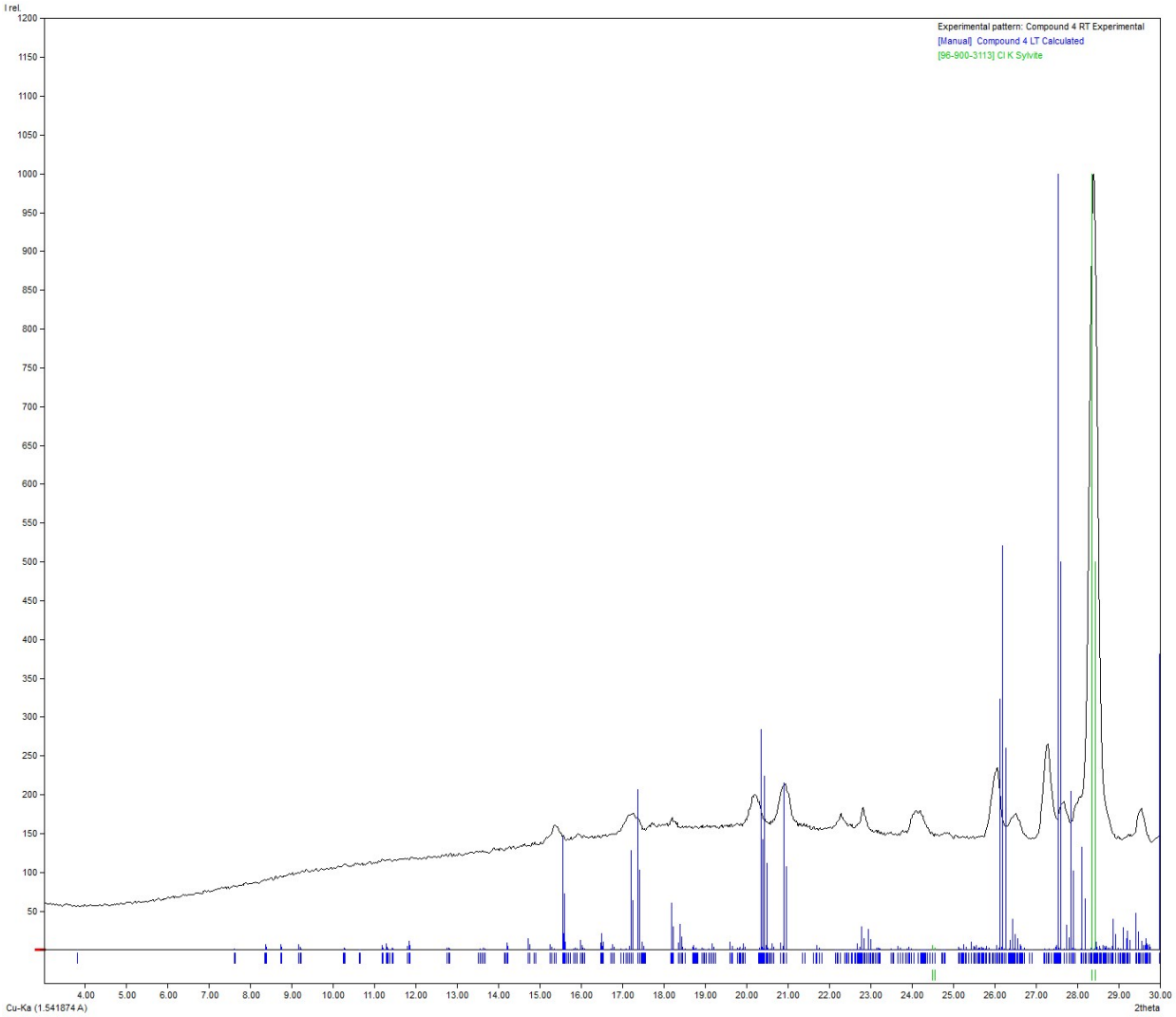

Figure S12: The PXRD pattern of the bulk product from the synthesis of **5** in black, which also produces known phase EDETEO.[1] The calculated pattern from 100(2) K SC-XRD data of **5** is overlaid in blue, and EDETEO in green. The PXRD pattern of the metathesis product of KSCN and $C_8H_{20}NCl$, which forms as a secondary product in the unoptimized synthesis of **5**, is shown in red.

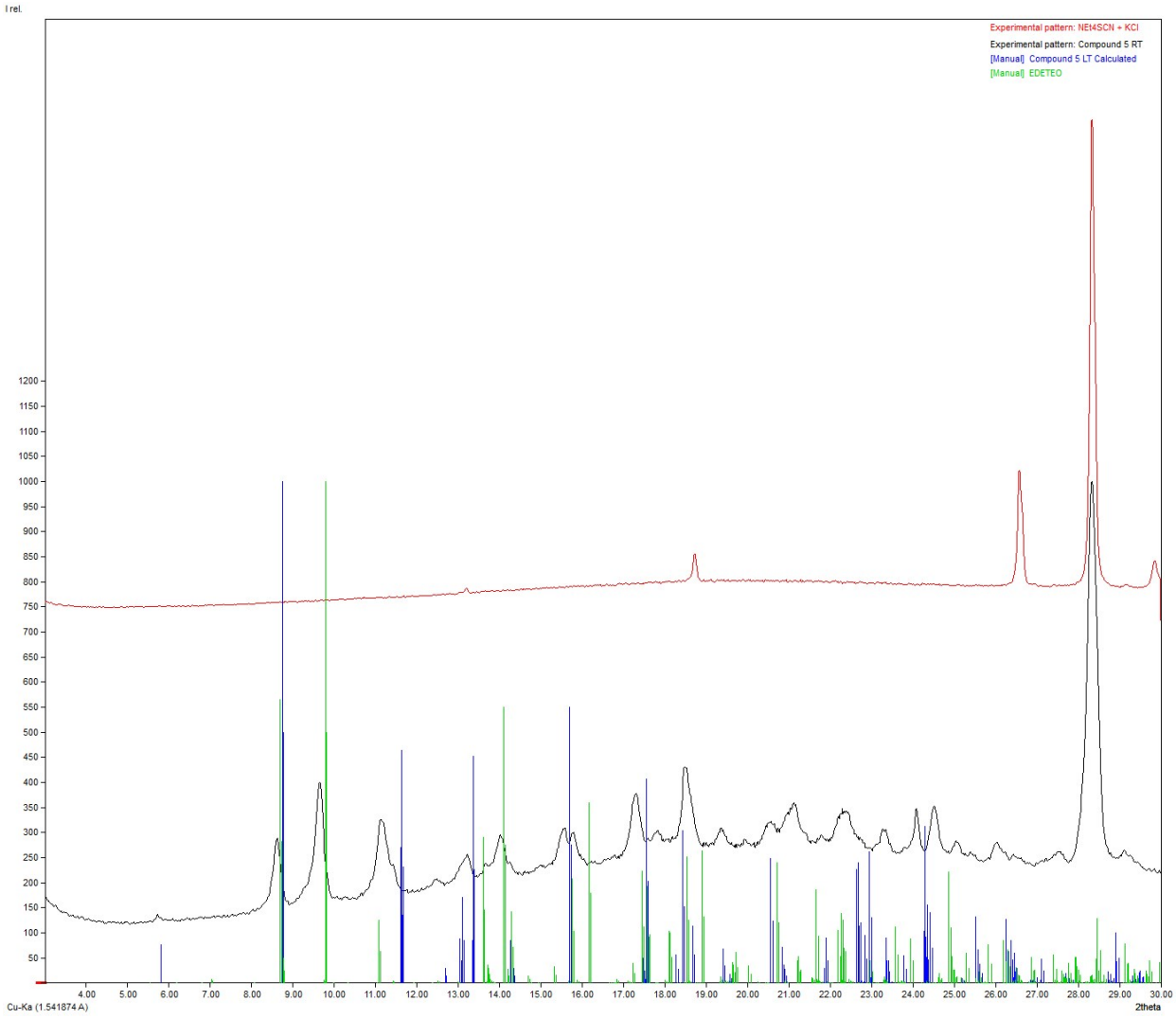

Figure S13: The PXRD pattern of the bulk product from the synthesis of **6** in black. The calculated pattern from 100(2) K SC-XRD data of **6** is overlaid in blue. The pattern of KCl is shown in green, which forms as a byproduct of KSCN and HCl.

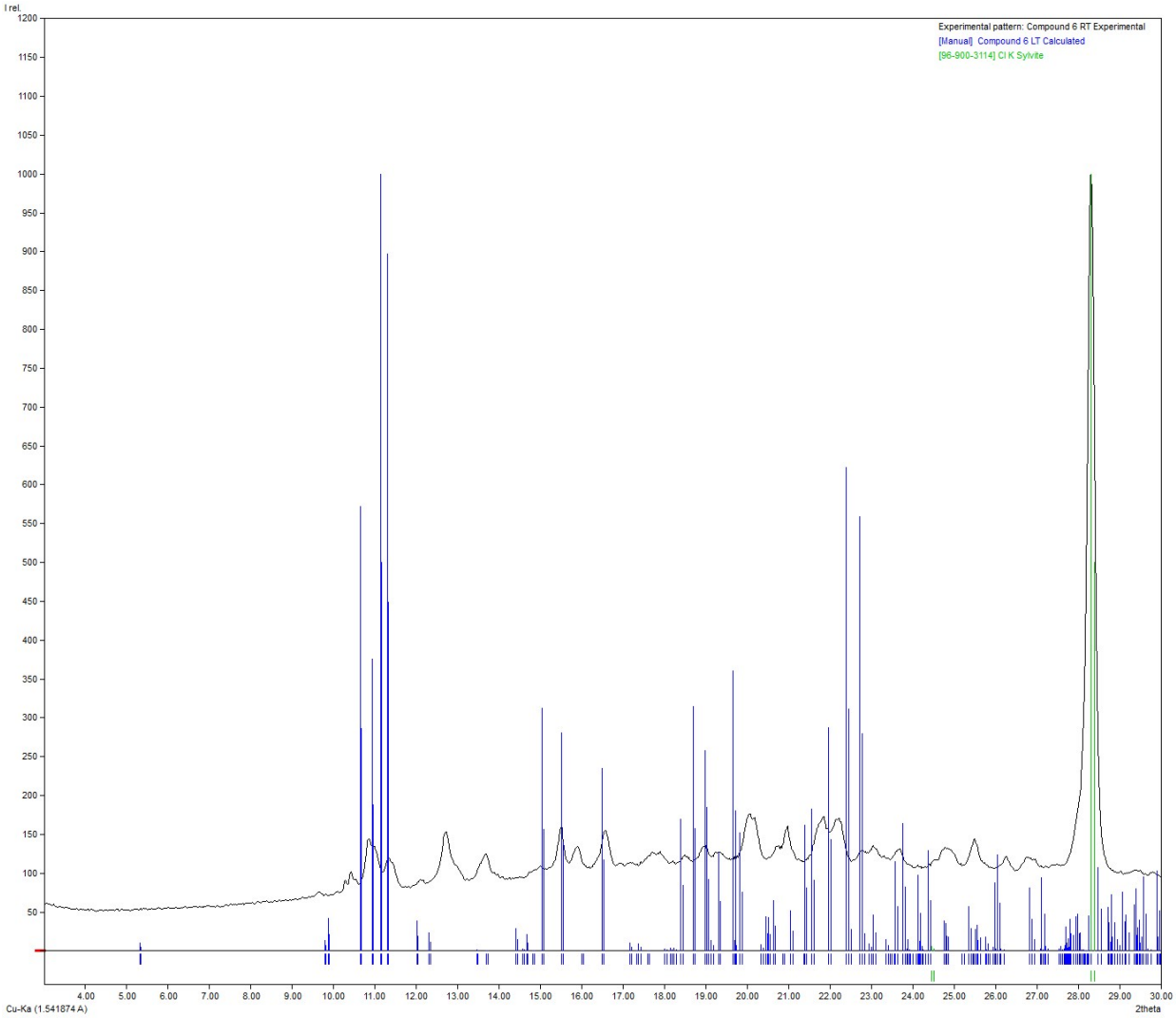

Figure S14: UV-Vis-DRS of compound **1** collected at room temperature.

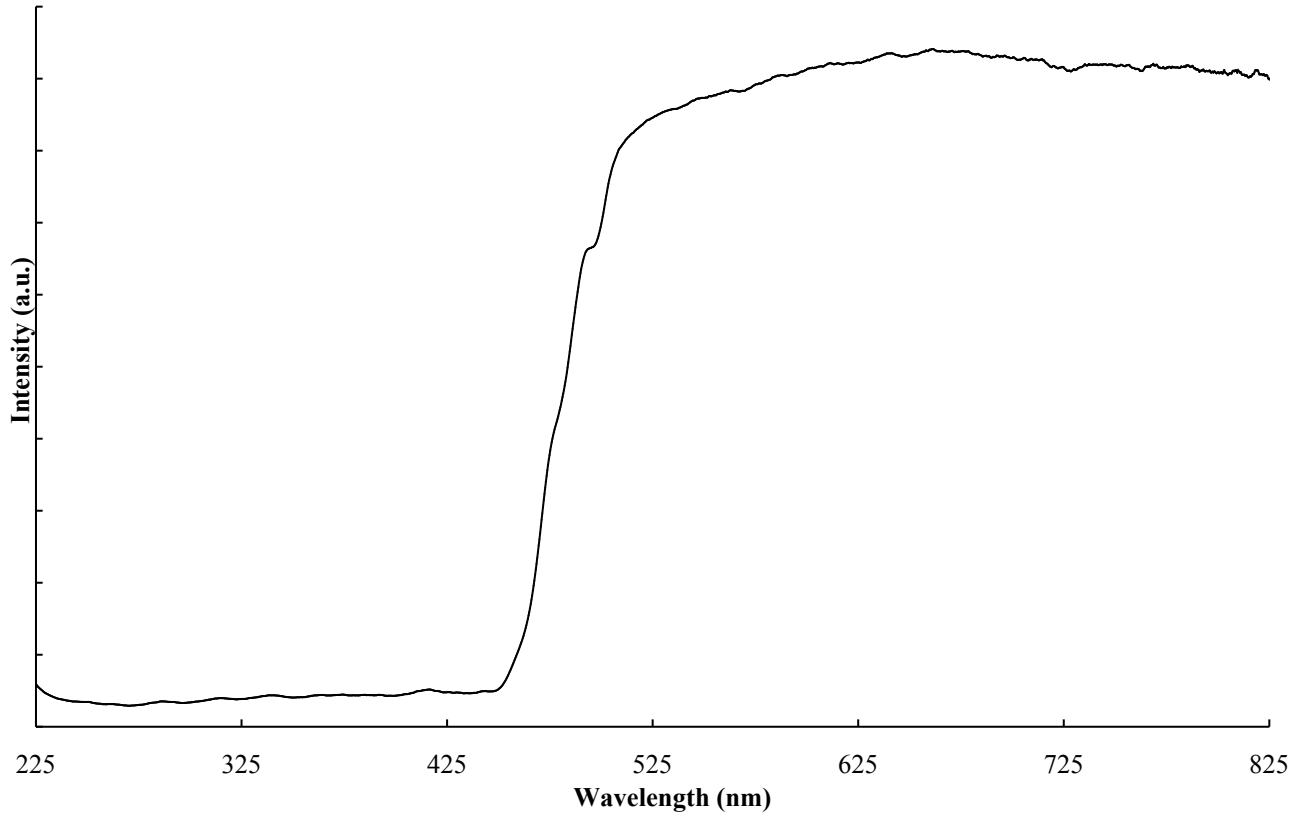

Figure S15: UV-Vis-DRS of compound **2** collected at room temperature.

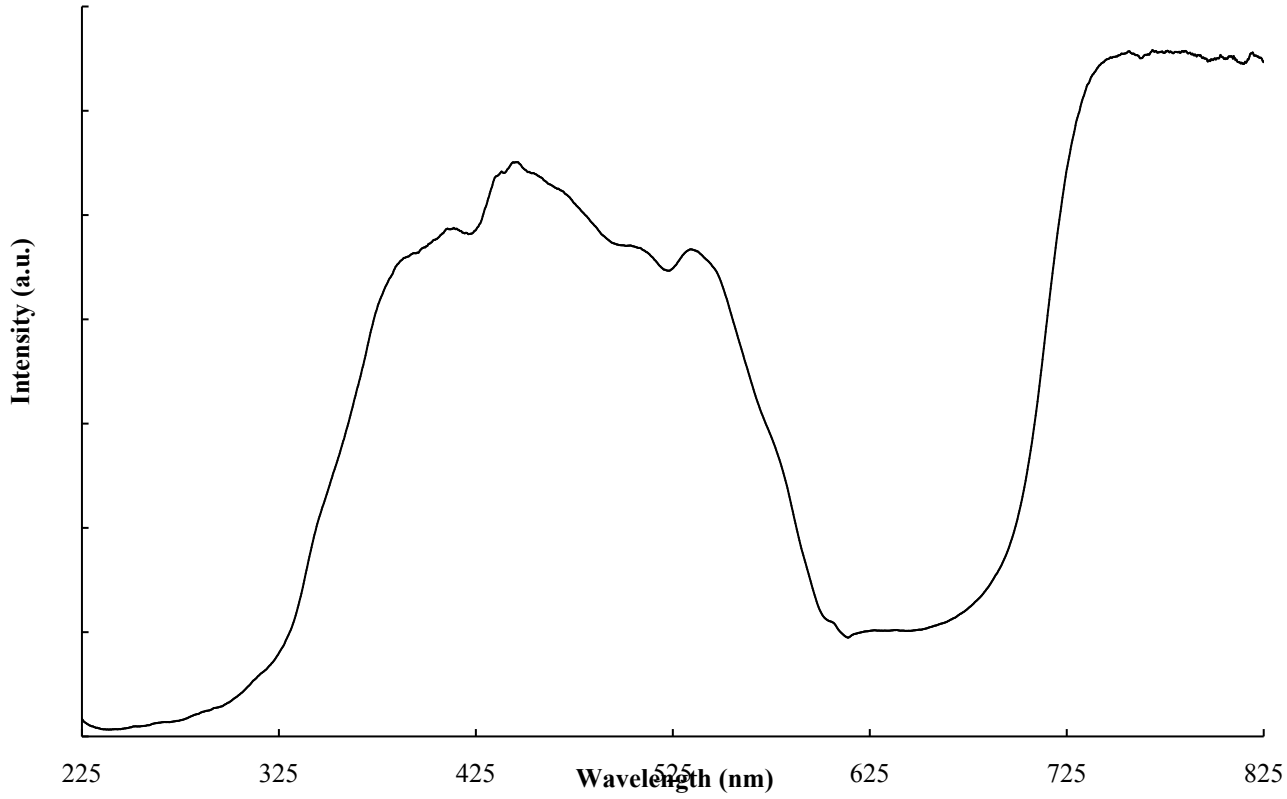

Figure S16: UV-Vis-DRS of compound **3** collected at room temperature.

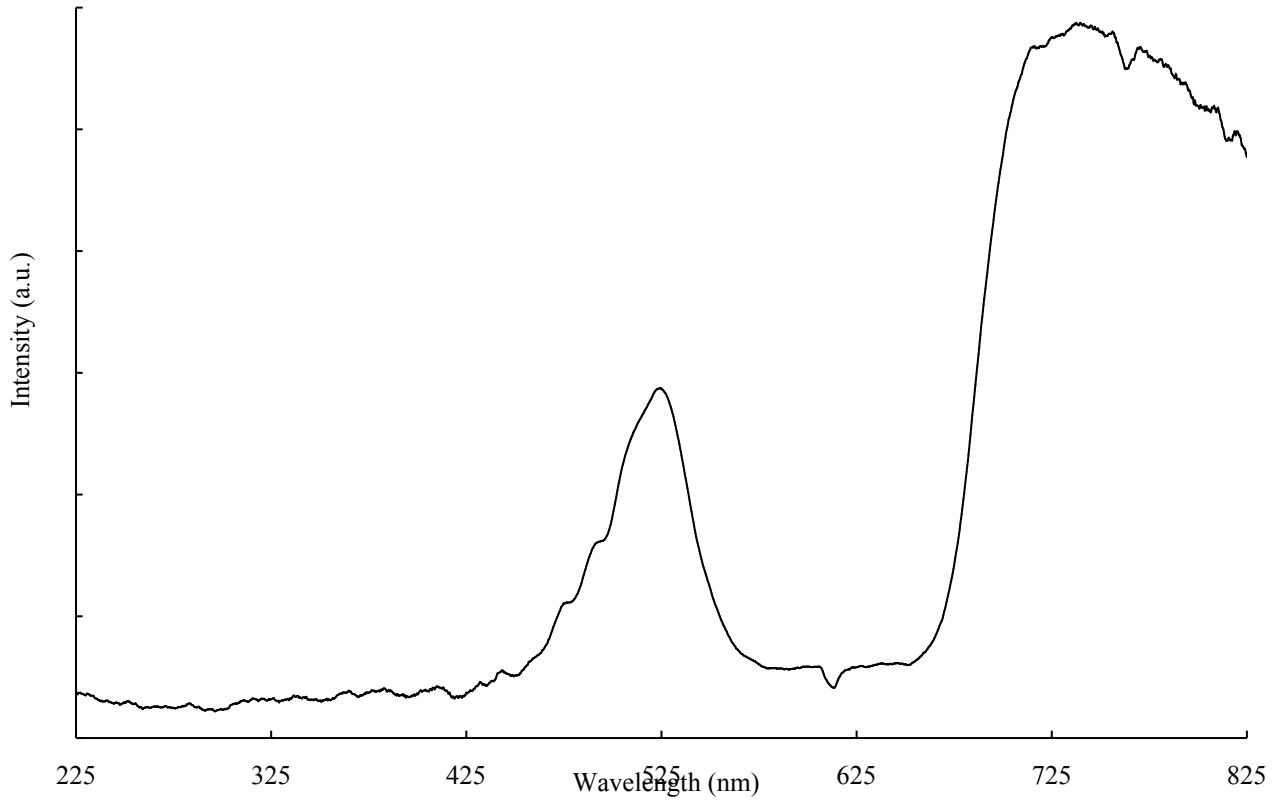

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Figure S17: Room temperatuer Raman spectrum of compound **1**.

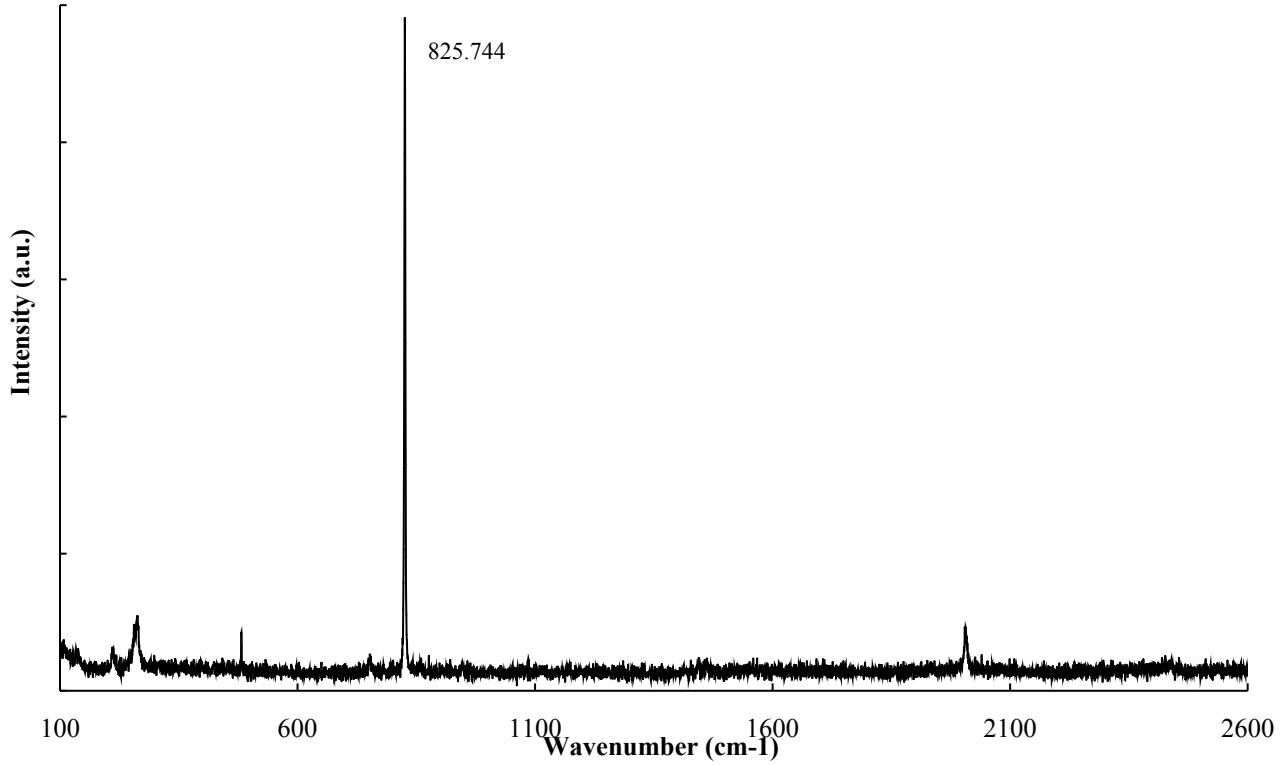


Figure S18: Room temperature Raman spectrum of compound **3**.

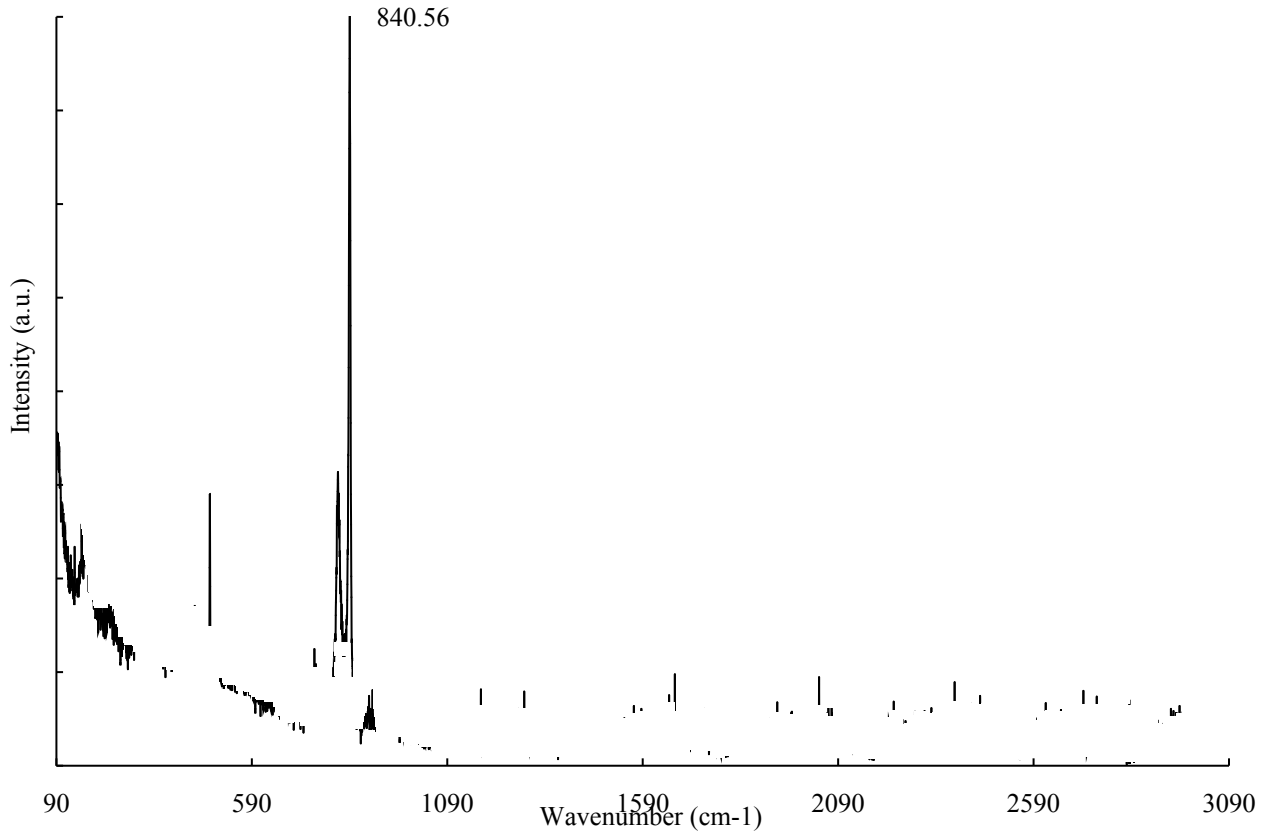


Figure S19: DFT calculated Raman spectra of (a) Model A, (b) Model B, (c) $[UO_2(NCS)_5]^{3-}$, and (d) $[Co(NCS)_4]^{2-}$ using B3LYP, between 200 cm^{-1} and 1500 cm^{-1}.

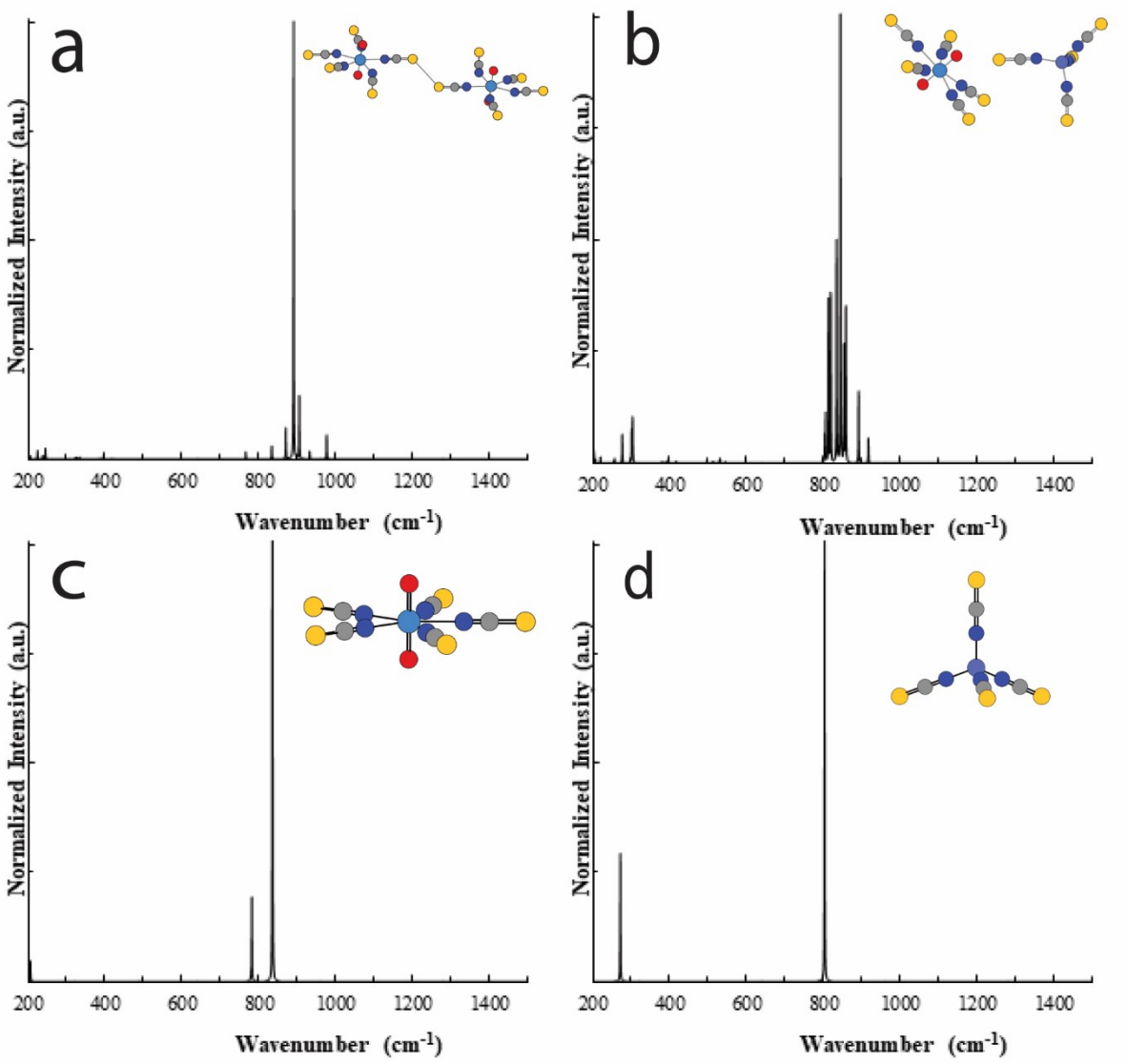


Table S10: Calculated Raman and IR frequencies and atomic displacements for Model A in the uranyl symmetric stretch region.

Frequency	866			904			904.3		
IR Intensity	4.79			15.5			7E-04		
Raman Intensity	4.42			0.01			104.6		
	X	Y	Z	X	Y	Z	X	Y	Z
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.33	0.36	-0.13	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	-0.02	-0.01	-0.01	0.36	0.16	0.01	-0.35	-0.16
N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	0.00
N	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N	0.39	0.46	-0.13	0.00	0.01	0.00	0.00	-0.01	0.00
N	0.00	-0.02	0.00	-0.03	0.47	0.09	0.03	-0.46	-0.09
O	0.00	0.00	0.06	-0.01	0.00	0.09	0.01	0.00	-0.09
O	0.01	0.00	-0.06	0.01	0.00	-0.13	-0.01	0.00	0.12
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	-0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	-0.26	-0.29	0.11	0.00	0.00	0.00	0.00	0.00	0.00
S	0.00	0.01	0.00	0.00	-0.30	-0.10	0.00	0.30	0.10
U	-0.01	-0.01	0.00	0.00	-0.01	0.00	0.00	0.01	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.16	0.18	-0.07	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	-0.01	0.00	-0.01	0.35	0.16	-0.01	0.36	0.16
N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	0.00
N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N	0.19	0.23	-0.06	0.00	0.01	0.00	0.00	0.01	0.00
N	0.00	-0.01	0.00	-0.03	0.46	0.09	-0.03	0.47	0.09
O	0.00	0.00	0.03	-0.01	0.00	0.09	-0.01	0.00	0.09
O	0.00	0.00	-0.03	0.01	0.00	-0.12	0.01	0.00	-0.12
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	-0.13	-0.14	0.05	0.00	0.00	0.00	0.00	0.00	0.00
S	0.00	0.01	0.00	0.00	-0.30	-0.10	0.00	-0.30	-0.10
U	0.00	0.00	0.00	0.00	-0.01	0.00	0.00	-0.01	0.00
Frequency	925			925			940.7		
IR Intensity	25.3			0			0		

Raman Intensity	0.06			337			212.5		
	X	Y	Z	X	Y	Z	X	Y	Z
C	0.16	0.01	0.02	-0.16	-0.01	-0.02	0.33	0.02	0.04
C	-0.01	0.03	0.00	0.01	-0.03	0.00	0.01	-0.05	0.00
C	0.02	0.00	0.01	-0.02	0.00	-0.01	-0.01	0.00	0.00
C	0.02	0.03	-0.01	-0.02	-0.03	0.01	-0.01	-0.02	0.01
C	0.00	0.07	0.03	0.00	-0.07	-0.03	0.00	-0.04	-0.02
N	0.22	0.02	0.04	-0.22	-0.02	-0.04	0.43	0.04	0.07
N	-0.02	0.05	0.00	0.02	-0.04	0.00	0.02	-0.07	-0.01
N	0.02	-0.01	0.00	-0.02	0.01	0.00	-0.01	0.01	0.00
N	0.03	0.03	0.00	-0.03	-0.03	0.00	-0.02	-0.02	0.00
N	-0.02	0.09	0.01	0.01	-0.08	-0.01	0.01	-0.05	-0.01
O	0.03	0.00	-0.35	-0.03	0.00	0.34	-0.01	0.00	0.16
O	-0.05	0.00	0.51	0.05	0.00	-0.50	0.03	0.00	-0.27
S	-0.15	-0.01	-0.02	0.15	0.01	0.02	-0.28	-0.02	-0.04
S	0.01	-0.04	0.00	-0.01	0.04	0.00	-0.01	0.05	0.00
S	-0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
S	-0.01	-0.02	0.01	0.01	0.01	-0.01	0.01	0.01	0.00
S	0.00	-0.05	-0.02	0.00	0.05	0.02	0.00	0.03	0.01
U	0.00	0.00	-0.01	0.00	0.00	0.01	-0.01	0.00	0.01
C	0.16	0.01	0.02	0.16	0.01	0.02	-0.33	-0.02	-0.04
C	-0.01	0.03	0.00	-0.01	0.03	0.00	-0.01	0.05	0.00
C	0.02	0.00	0.01	0.02	0.00	0.01	0.01	0.00	0.00
C	0.02	0.03	-0.01	0.02	0.03	-0.01	0.01	0.02	-0.01
C	0.00	0.07	0.03	0.00	0.07	0.03	0.00	0.04	0.02
N	0.22	0.02	0.04	0.22	0.02	0.04	-0.43	-0.04	-0.07
N	-0.02	0.05	0.00	-0.02	0.04	0.00	-0.02	0.07	0.01
N	0.02	-0.01	0.00	0.02	-0.01	0.00	0.01	-0.01	0.00
N	0.03	0.03	0.00	0.03	0.03	0.00	0.02	0.02	0.00
N	-0.02	0.09	0.01	-0.01	0.09	0.01	-0.01	0.05	0.01
O	0.03	0.00	-0.34	0.03	0.00	-0.35	0.01	0.00	-0.16
O	-0.05	0.00	0.50	-0.05	0.00	0.51	-0.03	0.00	0.27
S	-0.15	-0.01	-0.02	-0.15	-0.01	-0.02	0.28	0.02	0.04
S	0.01	-0.04	0.00	0.01	-0.04	0.00	0.01	-0.05	0.00
S	-0.01	0.00	0.00	-0.01	0.00	0.00	0.00	0.00	0.00
S	-0.01	-0.01	0.01	-0.01	-0.01	0.01	-0.01	-0.01	0.00
S	0.00	-0.05	-0.02	0.00	-0.05	-0.02	0.00	-0.03	-0.01
U	0.00	0.00	-0.01	0.00	0.00	-0.01	0.01	0.00	-0.01

Table S11: Calculated Raman and IR frequencies and atomic displacements for Model B in the uranyl symmetric stretch region.

Frequency	834.75			836.84			844.96		
IR Intensity	0.9128			1.4715			14.826		
Raman Intensity	21.7			35.225			54.788		
	X	Y	Z	X	Y	Z	X	Y	Z
U	0.00	-0.01	0.00	-0.01	0.00	0.01	0.00	0.00	0.00
Co	0.00	0.00	0.00	0.00	0.00	0.00	0.01	-0.03	-0.03
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.32	-0.28
S	0.00	0.00	0.00	0.00	0.00	0.00	-0.02	0.01	-0.02
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	-0.03	0.01	0.02	-0.32	0.11	0.28	0.00	0.00	0.00
S	0.21	-0.36	-0.15	-0.02	0.04	0.02	0.00	-0.01	0.00
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	0.02	0.03	-0.02	0.01	0.02	-0.01	-0.05	-0.08	0.05
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
O	-0.08	0.01	-0.07	-0.07	0.01	-0.08	-0.03	0.00	-0.03
O	0.07	0.00	0.07	0.07	-0.01	0.06	0.03	0.00	0.03
N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N	0.00	0.00	0.00	0.00	0.00	0.00	0.03	-0.01	0.03
N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.00
N	0.00	0.00	0.00	0.00	0.00	0.00	-0.04	0.50	0.44
N	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
N	-0.30	0.55	0.24	0.03	-0.06	-0.03	-0.01	0.01	0.00
N	-0.03	-0.05	0.03	-0.02	-0.04	0.02	0.08	0.12	-0.07
N	0.04	-0.01	-0.04	0.48	-0.17	-0.44	0.00	0.00	0.00
N	0.01	0.01	-0.01	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.42	0.38
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.02	-0.01	0.03
C	0.01	0.01	-0.01	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
C	0.03	-0.01	-0.03	0.41	-0.13	-0.36	0.00	0.00	0.00
C	-0.27	0.46	0.19	0.03	-0.05	-0.02	0.00	0.01	0.00
C	-0.02	-0.04	0.02	-0.02	-0.03	0.02	0.06	0.10	-0.05
Frequency	845.1			851.02			866.76		
IR Intensity	1.8503			27.352			2.1718		
Raman Intensity	58.058			113.9			184.8		
	X	Y	Z	X	Y	Z	X	Y	Z
U	0.00	-0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00
Co	0.00	0.01	0.01	-0.03	0.01	-0.04	0.00	0.00	0.00
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

S	0.00	0.08	0.07	0.00	0.02	0.02	0.00	0.00	0.00
S	0.01	0.00	0.01	-0.27	0.09	-0.32	0.00	0.00	0.00
S	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
S	-0.01	0.00	0.01	0.00	0.00	0.00	0.03	-0.01	-0.02
S	0.01	-0.02	-0.01	0.00	0.00	0.00	-0.01	0.02	0.01
S	0.00	0.00	0.00	0.00	0.00	0.00	0.23	0.18	-0.24
S	-0.20	-0.33	0.19	0.00	0.00	0.00	0.02	0.04	-0.02
S	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.05	0.00
O	-0.11	0.01	-0.11	0.00	0.00	0.00	-0.28	0.03	-0.27
O	0.10	-0.01	0.10	0.00	0.00	0.00	0.24	-0.03	0.24
N	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	0.00	0.00
N	-0.01	0.00	-0.01	0.42	-0.14	0.53	0.00	0.00	0.00
N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N	0.01	-0.13	-0.11	0.00	-0.03	-0.03	0.00	0.00	0.00
N	0.00	-0.01	0.00	0.00	0.00	0.00	-0.02	-0.07	-0.01
N	-0.02	0.03	0.01	0.00	0.00	0.00	0.02	-0.04	-0.02
N	0.31	0.50	-0.30	0.00	0.00	0.00	-0.04	-0.06	0.04
N	0.02	-0.01	-0.02	0.00	0.00	0.00	-0.04	0.02	0.04
N	-0.01	0.00	0.01	0.00	0.00	0.00	-0.36	-0.26	0.37
C	0.00	0.00	0.00	-0.01	0.00	0.00	0.00	0.00	0.00
C	0.00	-0.11	-0.10	0.00	-0.03	-0.03	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	-0.01	0.00	-0.01	0.37	-0.13	0.43	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	-0.29	-0.23	0.29
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.05	0.00
C	0.02	-0.01	-0.01	0.00	0.00	0.00	-0.04	0.01	0.04
C	-0.01	0.02	0.01	0.00	0.00	0.00	0.02	-0.03	-0.01
C	0.23	0.41	-0.21	0.00	0.00	0.00	-0.03	-0.06	0.03
Frequency IR Intensity Raman Intensity	877.14 0.2943 325.84			886.84 13.434 86.645			891.86 0.7567 112.9		
	X	Y	Z	X	Y	Z	X	Y	Z
U	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-0.01	0.00
Co	0.00	0.00	0.00	-0.01	-0.05	0.02	0.00	0.00	0.00
S	0.00	0.00	0.00	-0.04	-0.40	0.13	0.00	-0.01	0.00
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
S	-0.03	0.01	0.03	0.00	0.00	0.00	0.02	-0.01	-0.02
S	0.02	-0.03	-0.01	0.00	0.00	0.00	-0.01	0.02	0.01
S	0.13	0.10	-0.13	0.00	0.00	0.00	-0.05	-0.04	0.06
S	-0.02	-0.04	0.02	0.00	0.00	0.00	0.02	0.03	-0.01
S	-0.05	-0.24	-0.02	0.00	0.01	0.00	-0.08	-0.36	-0.03
O	0.35	-0.04	0.35	0.00	0.00	0.00	-0.27	0.03	-0.27
O	-0.31	0.03	-0.31	0.00	0.00	0.00	0.23	-0.02	0.23

N	-0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00
N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N	0.00	0.01	0.00	0.10	0.67	-0.23	0.00	0.01	0.00
N	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N	0.09	0.37	0.03	0.00	-0.02	0.00	0.13	0.59	0.05
N	-0.03	0.06	0.03	0.00	0.00	0.00	0.02	-0.04	-0.02
N	0.04	0.08	-0.04	0.00	0.00	0.00	-0.03	-0.05	0.03
N	0.05	-0.02	-0.05	0.00	0.00	0.00	-0.05	0.02	0.04
N	-0.21	-0.15	0.22	0.00	0.00	0.00	0.09	0.06	-0.10
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.01	0.00	0.05	0.52	-0.18	0.00	0.01	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	-0.18	-0.14	0.18	0.00	0.00	0.00	0.08	0.06	-0.08
C	0.03	0.26	0.01	0.00	-0.01	0.00	0.06	0.43	0.02
C	0.05	-0.02	-0.04	0.00	0.00	0.00	-0.04	0.01	0.04
C	-0.03	0.06	0.02	0.00	0.00	0.00	0.02	-0.04	-0.02
C	0.04	0.06	-0.03	0.00	0.00	0.00	-0.02	-0.04	0.02

Figure S20: Room temperature IR spectra of compound **1**.

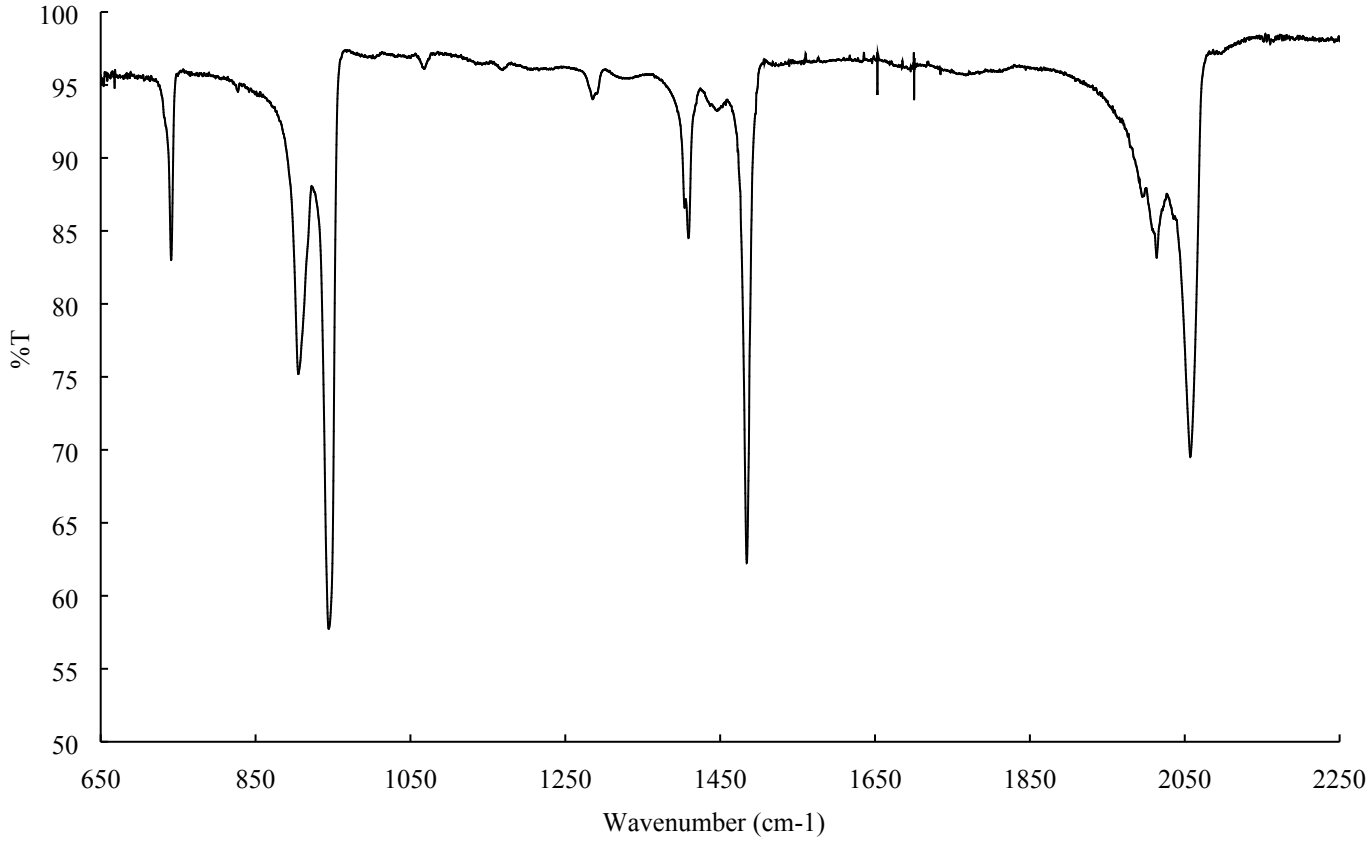


Figure 21: Room temperature IR spectra of compound **3**.

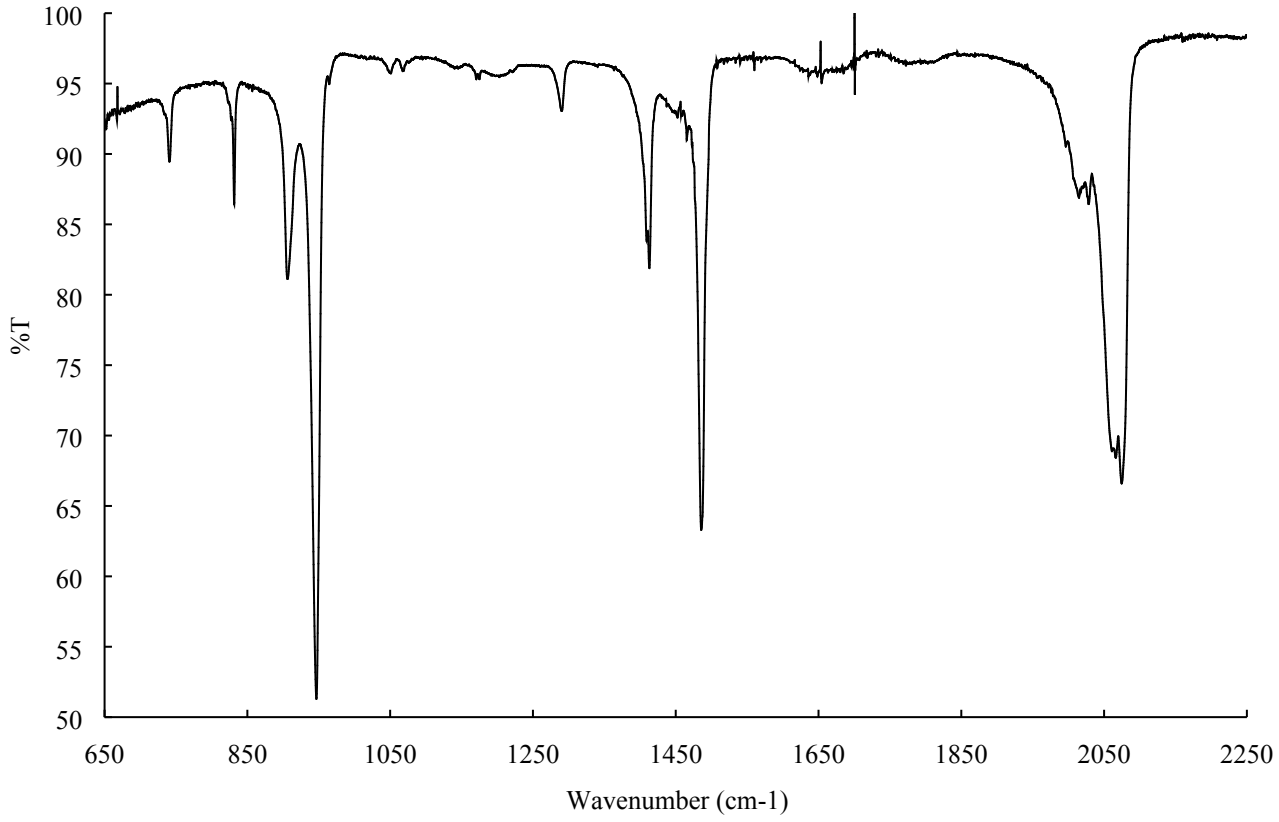
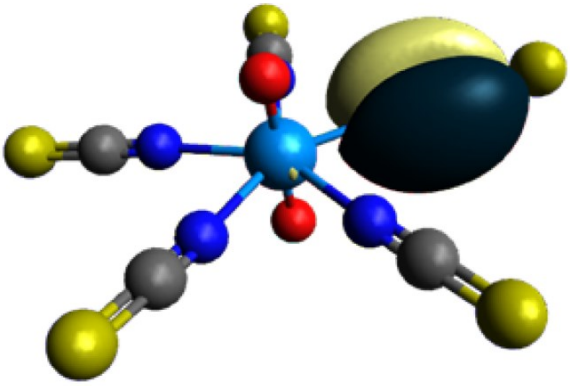


Figure 22: Isodensity representation of the HOMO and LUMOs present in the geometry optimized $[UO_2(NCS)_5]^{3-}$ anion.

HOMO



LUMO

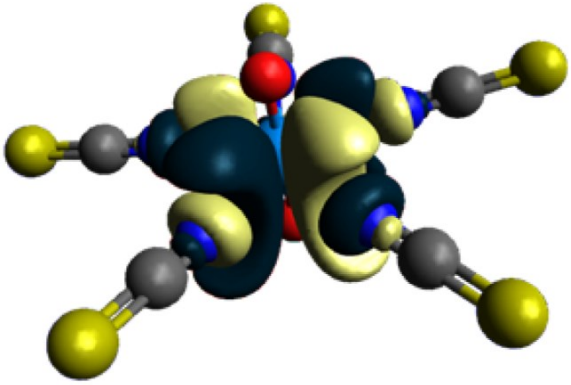


Figure S23: Isodensity representation of the HOMO and LUMOs present in the geometry optimized $[Co(NCS)_4]^{2-}$ anion.

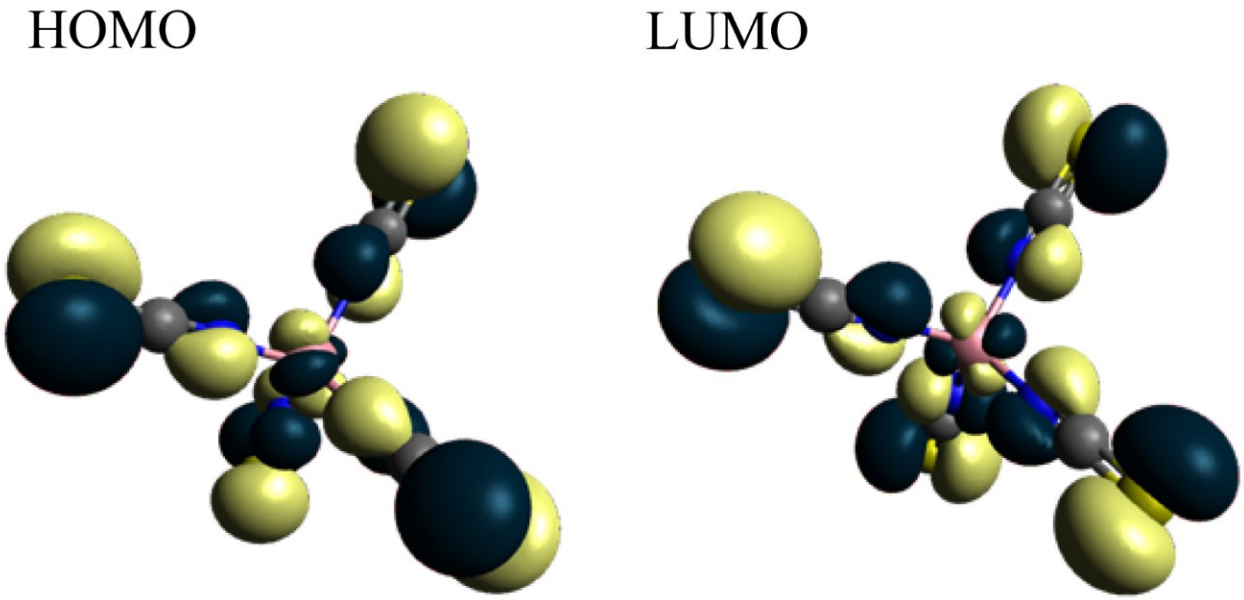


Figure S24: Homometallic $[UO_2(NCS)_5]^{6-}$ Model A, exhibiting S···S interactions between uranyl units, with relevant atoms labeled.

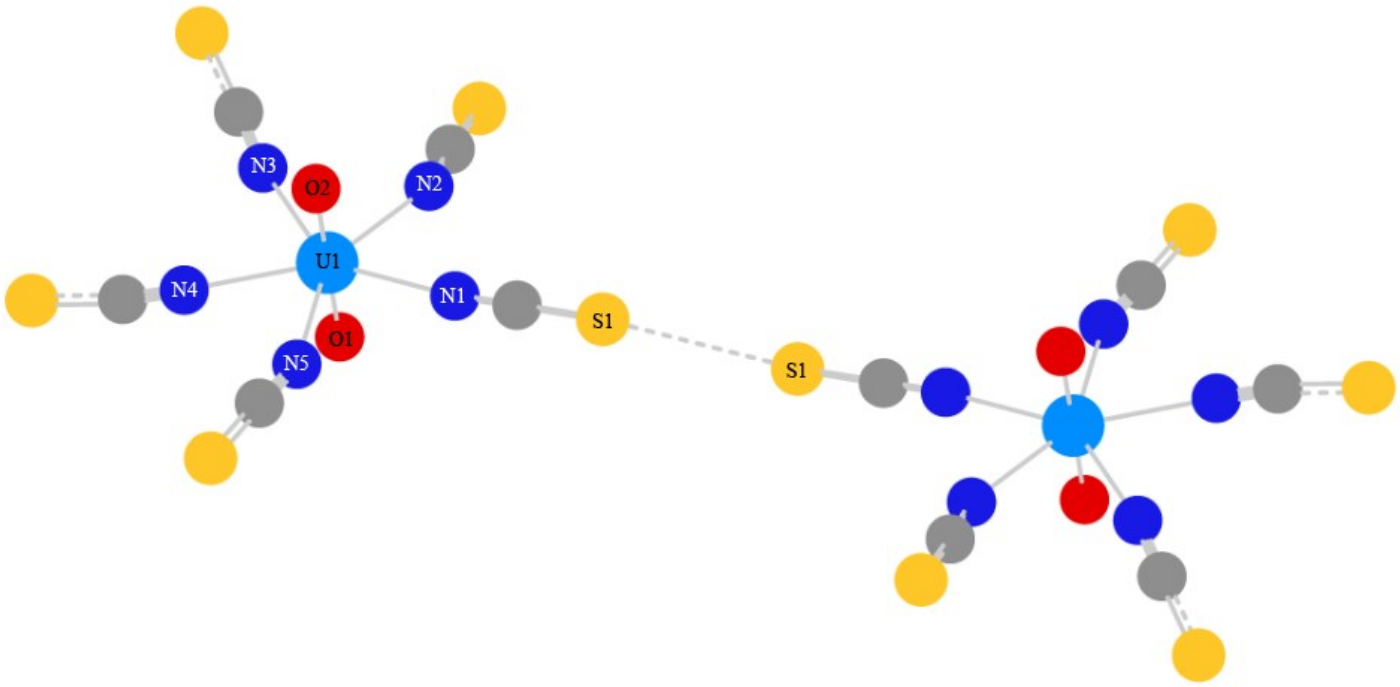


Figure S25: Heterometallic $[(Co(NCS)_4)(UO_2(NCS)_5]^{5-}$ Model B, exhibiting S···O_{yl} interactions between $[UO_2(NCS)_5]^{3-}$ and $[Co(NCS)_4]^{2-}$ units, with relevant atoms labeled.

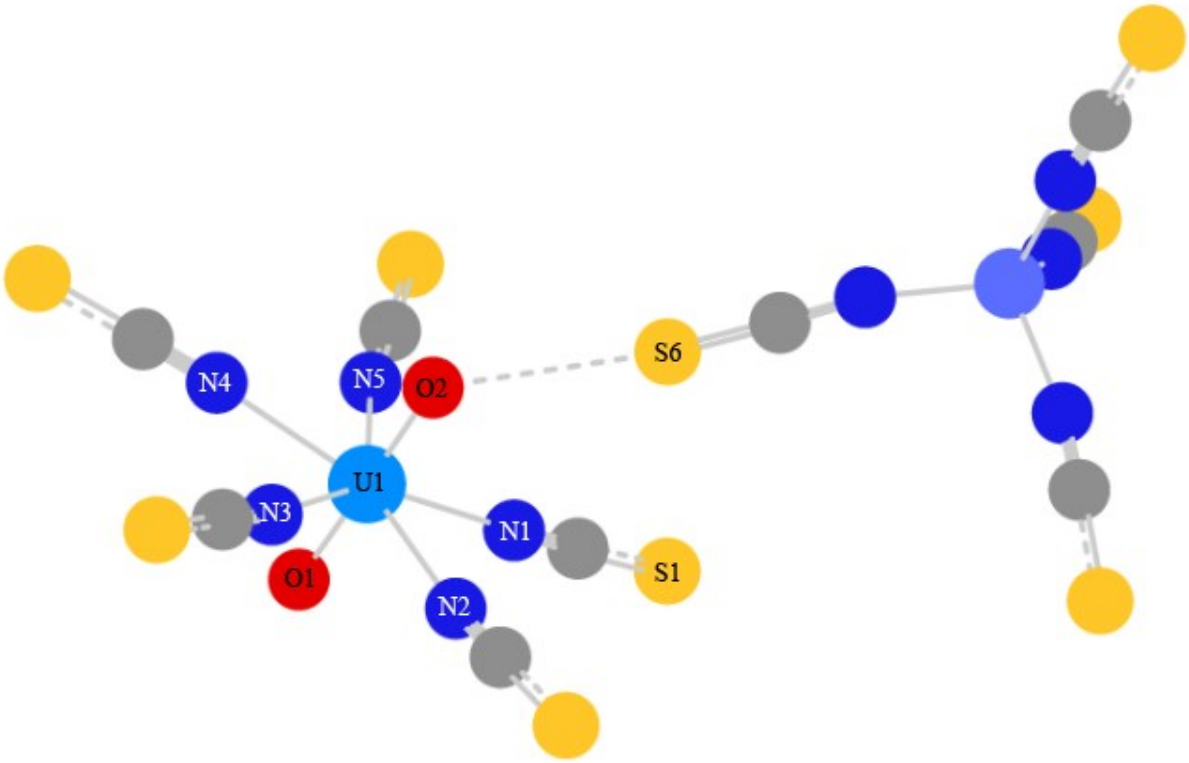


Figure S26: Isodensity representation of natural localized molecular orbital (NLMOs) involved in a U=O π-bonding interaction, common to both Model A and Model B.

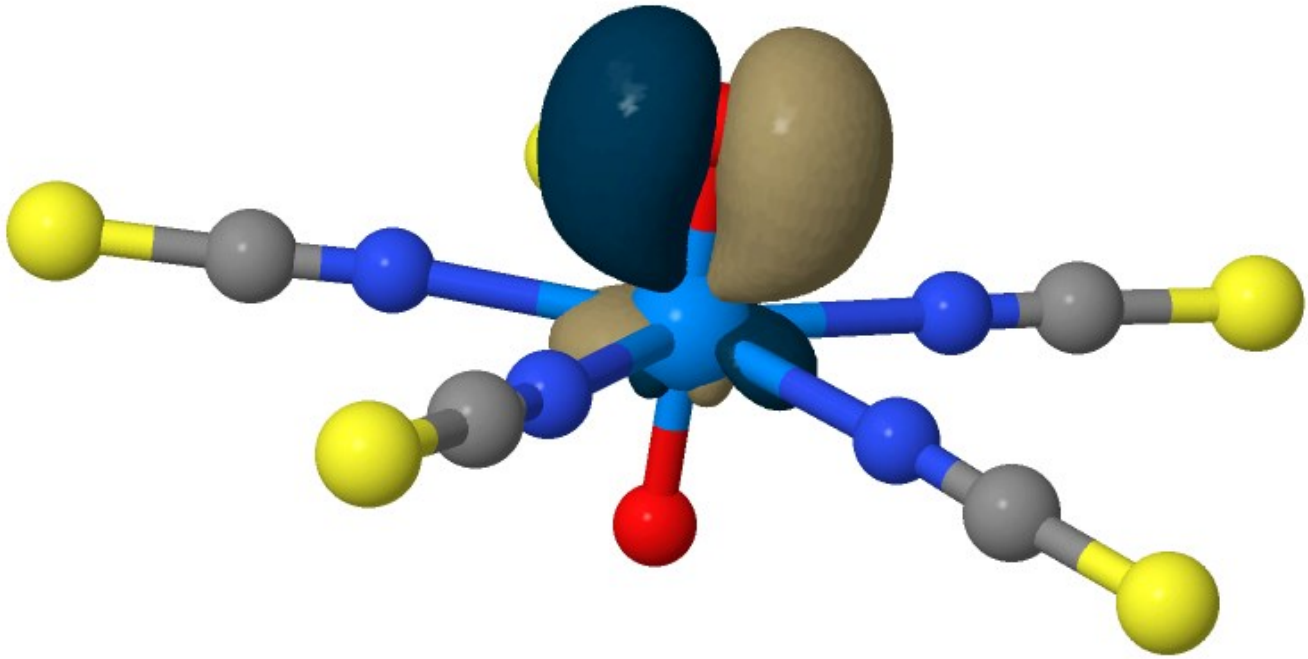


Figure S27: Isodensity representation of natural localized molecular orbital (NLMOs) involved in a U=O π-bonding interaction, common to both Model A and Model B.

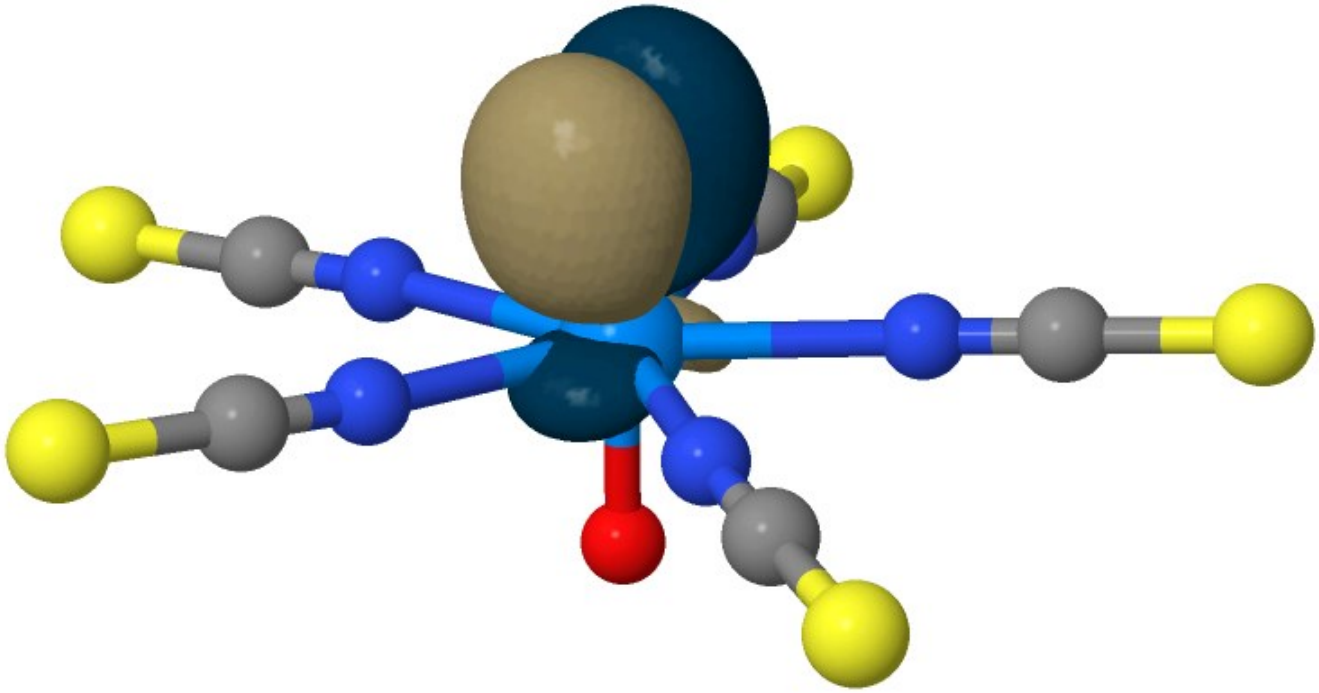


Figure S28: Isodensity representation of natural localized molecular orbital (NLMOs) involved in a U=O σ-bonding interaction, common to both Model A and Model B.

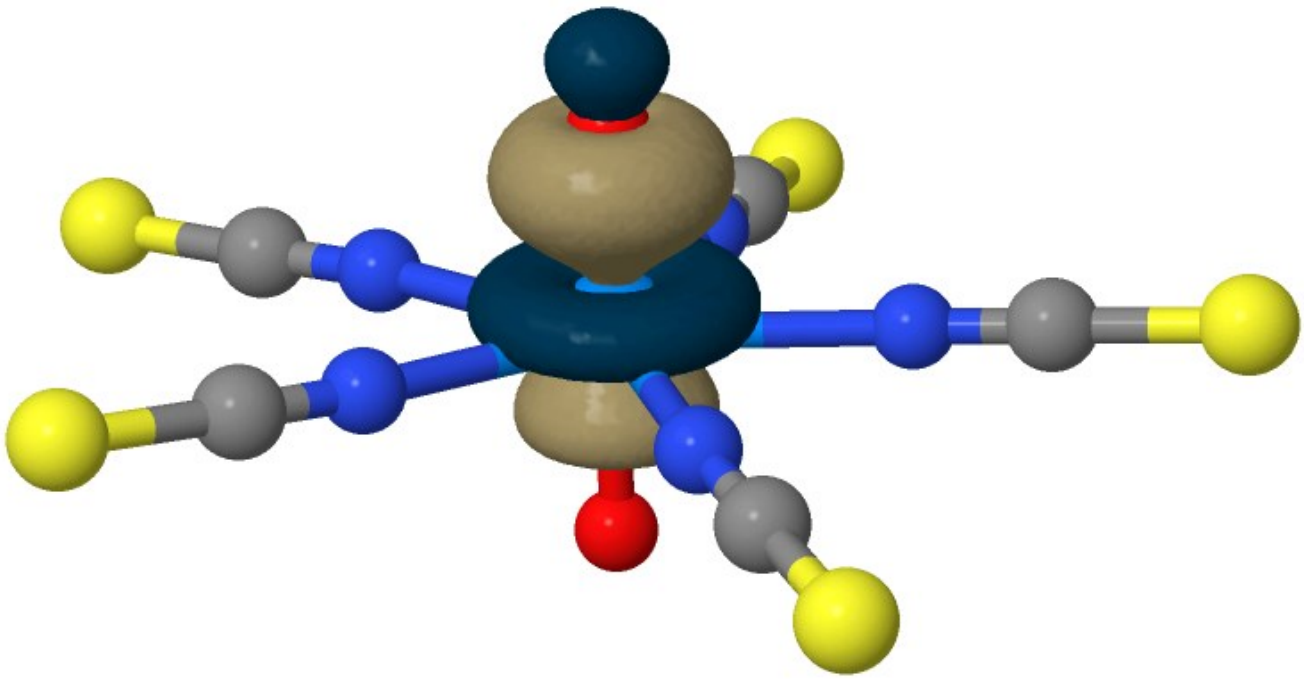


Table S12: Stabilization energies of U=O σ- and π- bonding interactions present in $[UO_2(NCS)_5]^{3-}$, Model A, and Model B, derived from SOPT analysis.

		Stabilization E (kcal/mol)		
Donor Orbital	**Acceptor Orbital**	**$[UO_2(NCS)_5]^{3-}$**	**Model A**	**Model B**
U1-O1 π	U1-O2 π*	2.77	0.75	0.83
U1-O1 π	U1-O2 π*	-	1.91	0.52
U1-O1 π	U1-O2 π*	2.77	0.74	0.53
U1-O1 π	U1-O2 π*	-	1.91	0.83
U1-O1 σ	U1-O2 σ*	37.96	37.14	17.52
U1-O2 π	U1-O1 π*	2.77	0.76	0.81
U1-O2 π	U1-O1 π*	-	1.89	0.52
U1-O2 π	U1-O1 π*	-	1.9	0.52
U1-O2 π	U1-O1 π*	2.77	0.7	0.83
U1-O2 σ	U1-O1 σ*	37.96	37.91	18.61
U1-O1 σ	U1-O1 σ*	11.51	10.72	5.16
U1-O2 σ	U1-O2 σ*	11.51	10.73	5.68

Table S13: Stabilization energies of S···S interactions in Model A derived from SOPT analysis.

Donor Orbital	Acceptor orbital	Stabilization Energy (kcal/mol)
LP S1a	C1b-S1b σ*	0.12
LP S1a	C1b-S1b σ*	0.21
LP S1a	C1b-S1b σ*	0.24
LP S1b	C1b-S1a σ*	0.12
LP S1b	C1b-S1a σ*	0.21
LP S1b	C1b-S1a σ*	0.24

Table S14: Stabilization energies of S···O_{yl} interactions in Model B derived from SOPT analysis.

Donor orbital	Acceptor orbital	Stabilization Energy (kcal/mol)
LP S6	U1-O2 σ*	0.13
LP S6	U1-O2 π*	0.04
LP S6	U1-O2 σ*	0.06
LP O2	S6-C23 σ*	0.11

Figure S29: Isodensity representation of NLMOs involved in S···S interactions between $[UO_2(NCS)_5]^{3-}$ anions, in which (left) S of unit 1 donates a lone pair (LP) electrons (e-) to the S=C σ* of unit 2 (right).

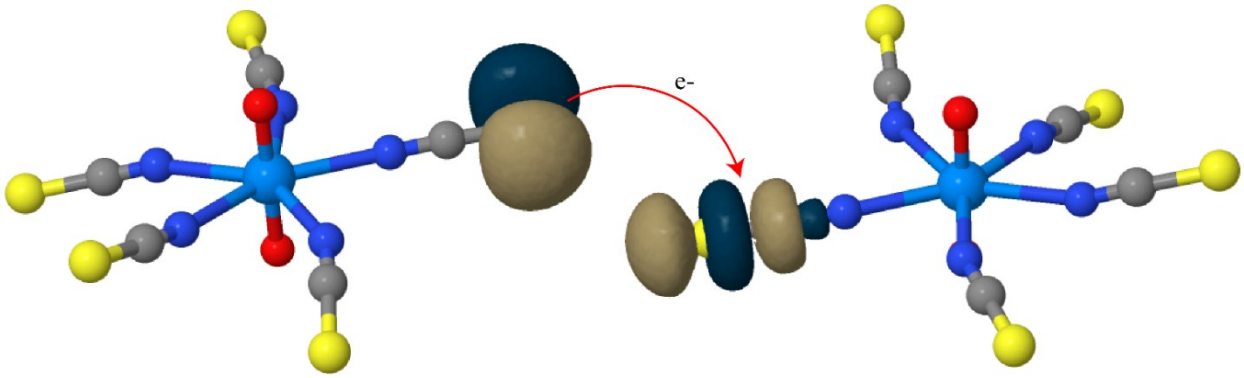


Figure S30: Isodensity representation of NLMOs involved in equivalent, yet opposite, S···S interaction between $[UO_2(NCS)_5]^{3-}$ anions, in which (left) S of unit 2 donates lone pair (LP) electrons (e-) to the S=C σ* of unit 1 (right).

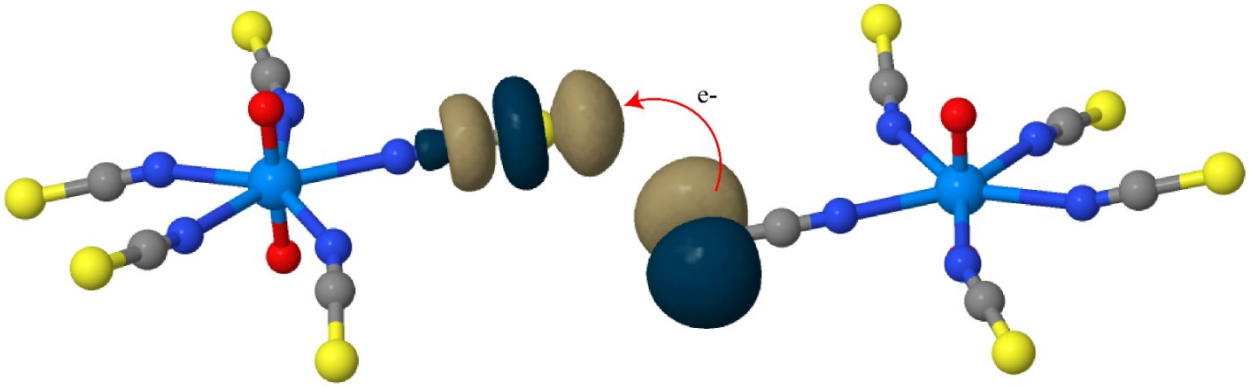


Figure S31: Isodensity representation of NLMOs involved in S···O_{yl} interaction, with S donating LP electrons (e-) to an acceptor U=O σ* orbital.

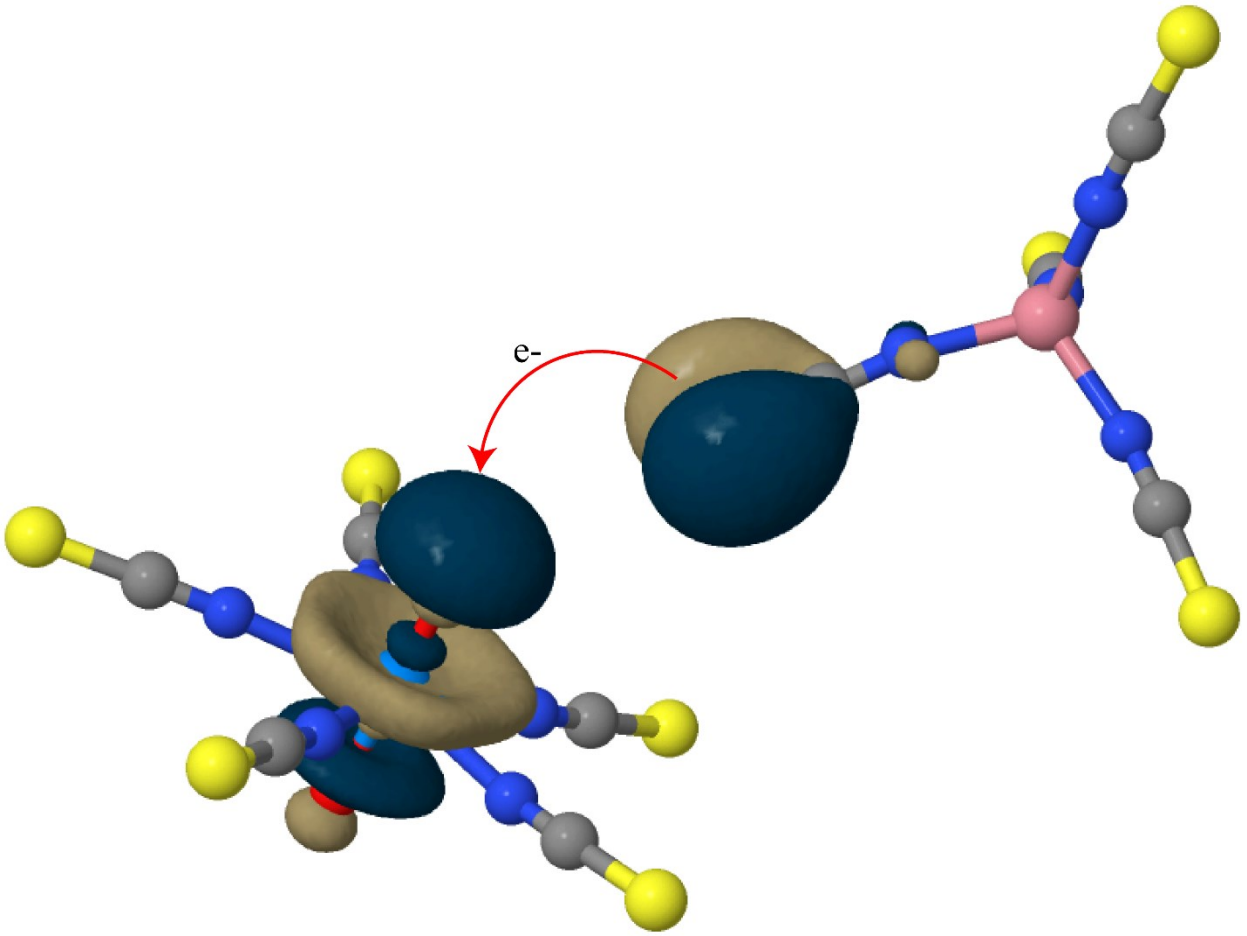


Figure S32: Isodensity representation of NLMOs involved in the back donation of the S···O_{yl} interaction, in which O LP electrons (e-) are donated to a C=S σ* orbital.

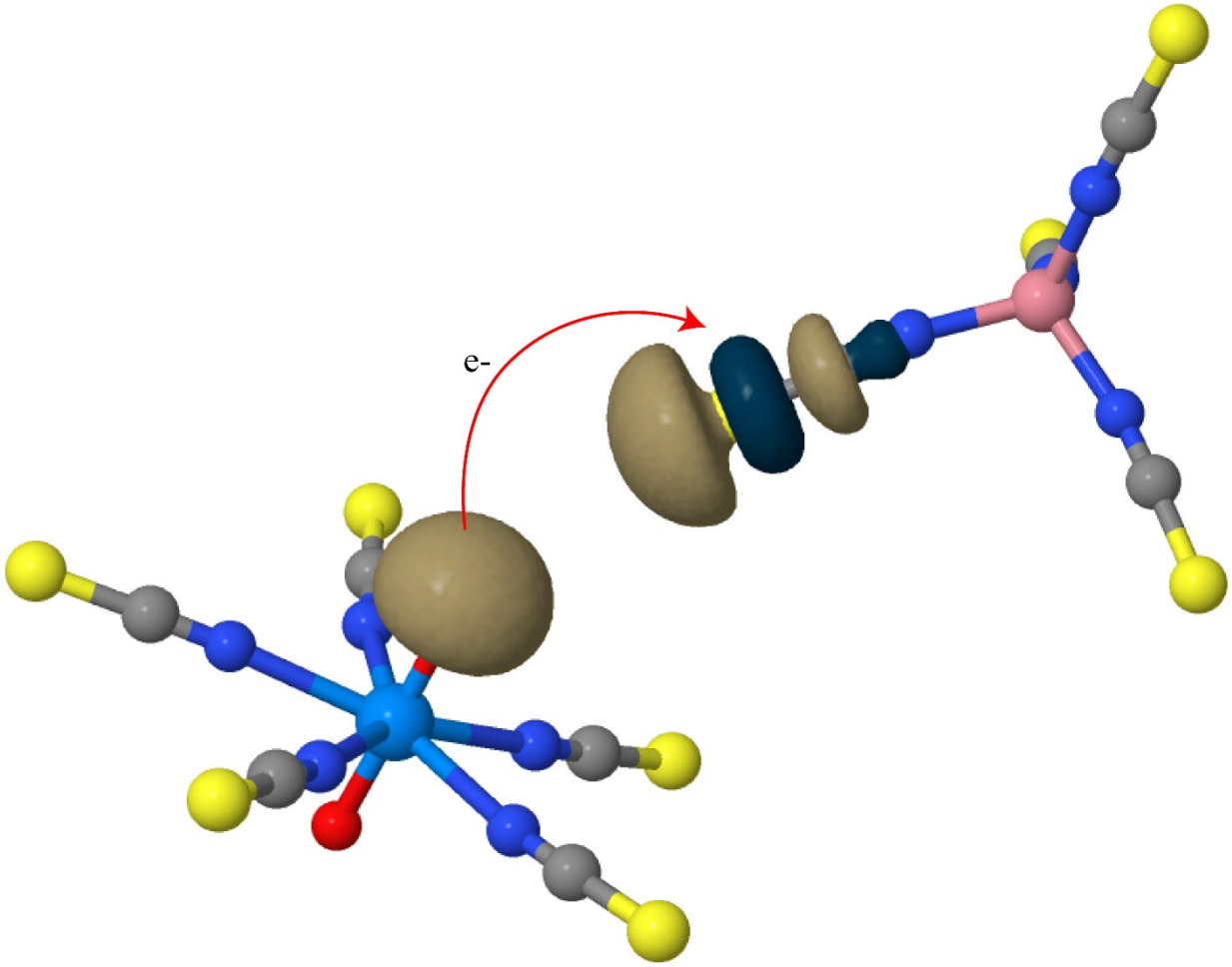


Table S15: Parent atom composition of U=O bonds within $[UO_2(NCS)_5]^{3-}$, Model A (with S···S interactions), and Model B (with S···O_{yl} interactions), derived from NBO analysis.

	$[UO_2(NCS)_5]^{3-}$		Model A		Model B	
	% U	% O	% U	% O	% U	% O
U-O1 (π)	21.34	78.31	21.33	78.34	21.02	78.63
U-O1 (π)	21.36	78.27	21.24	78.42	21.02	78.61
U-O1 (σ)	29.31	68.90	29.92	68.17	28.85	69.33
U-O2 (π)	21.37	78.30	21.25	78.42	21.76	77.89
U-O2 (π)	21.38	78.29	21.37	78.28	21.68	77.99
U-O2 (σ)	29.42	68.76	29.77	68.33	29.93	68.19

Table S16: Hybridization of U atomic orbitals involved in σ- and π-bonding interactions of Model A and Model B, derived from NBO analysis.

	Model A			Model B (O2)			Model B (O1)		
	σ (%)	π (%)	π (%)	σ (%)	π (%)	π (%)	σ (%)	π (%)	π (%)
s	0.14	0.00	0.01	0.13	0.00	0.00	0.13	0.00	0.01
p	0.29	0.08	0.09	0.30	0.09	0.09	0.23	0.06	0.06
d	17.09	37.66	37.86	17.62	37.89	37.88	17.00	37.20	37.50
f	82.44	62.21	62.00	81.90	61.97	61.98	82.61	62.69	62.38

Table S17: Wiberg bond order analysis of U=O bonds in $[UO_2(NCS)_5]^{3-}$, Model A, and Model B, at the bond critical point.

Atom(s)	$[UO_2(NCS)_5]^{3-}$	Model A	Model B
U=O1	2.080	2.089	2.057
U=O2	2.080	2.082	2.103
Average U=O	2.080	2.086	2.080

Table S18: Wiberg bond order analysis of U-N bonds in $[UO_2(NCS)_5]^{3-}$, Model A, and Model B.

Atom(s)	$[UO_2(NCS)_5]^{3-}$	Model A	Model B
U-N1	0.428	0.514	0.461
U-N2	0.428	0.453	0.461
U-N3	0.428	0.421	0.427
U-N4	0.428	0.433	0.443
U-N5	0.428	0.467	0.475
Average U-N	0.428	0.458	0.454

Table S19: Wiberg bond order analysis of all bonds within $[UO_2(NCS)_5]^{3-}$ across all models.

Atom(s)	$[UO_2(NCS)_5]^{3-}$	Model A	Model B
U=O1	2.080	2.089	2.057
U=O2	2.080	2.082	2.103
Average U-O	2.080	2.085	2.080
U-N1	0.428	0.514	0.461
U-N2	0.428	0.453	0.461
U-N3	0.428	0.421	0.427
U-N4	0.428	0.433	0.443
U-N5	0.428	0.467	0.475
Average U-N	0.428	0.458	0.454
C-S1	1.480	1.604	1.450
C-S2	1.480	1.517	1.478
C-S3	1.480	1.413	1.505
C-S4	1.480	1.464	1.475
C-S5	1.480	1.500	1.541
Average C-S	1.480	1.500	1.490
C-N1	2.457	2.332	2.424
C-N2	2.457	2.420	2.397
C-N3	2.457	2.508	2.478
C-N4	2.457	2.465	2.448
C-N5	2.457	2.425	2.462
Average C-N	2.457	2.430	2.442
S···S	-	0.007	-
S···Oyl	-	-	0.005

Table S20: Method validation across various functionals for Model A, using Wiberg bond orders as a comparative metric. (σ = 1.2-2.4%)

	B3LYP	BLYP	CAM-B3LYP	M062X	TPSSH	Standard Deviation (σ)
U=O1	2.089	2.107	2.087	2.079	2.104	-
U=O2	2.082	2.100	2.080	2.071	2.097	-
U=O Average	2.085	2.104	2.084	2.075	2.101	0.012
U-N1	0.514	0.559	0.489	0.465	0.530	-
U-N2	0.453	0.478	0.440	0.423	0.462	-
U-N3	0.421	0.442	0.410	0.395	0.428	-
U-N4	0.433	0.457	0.421	0.405	0.442	-
U-N5	0.467	0.495	0.452	0.434	0.477	-
U-N Average	0.458	0.486	0.442	0.424	0.468	0.024

Table S21: Method validation across various functionals for Model B, using Wiberg bond orders as a comparative metric. (σ = 1.2-2.4%)

	B3LYP	BLYP	CAM-B3LYP	M062X	TPSSH	Standard Deviation (σ)
U=O1	2.057	2.078	2.055	2.045	2.074	-
U=O2	2.103	2.117	2.103	2.094	2.119	-
U=O Average	2.080	2.097	2.079	2.069	2.096	0.012
U-N1	0.461	0.493	0.444	0.426	0.472	-
U-N2	0.461	0.492	0.444	0.427	0.472	-
U-N3	0.427	0.452	0.413	0.398	0.435	-
U-N4	0.443	0.468	0.430	0.414	0.452	-
U-N5	0.475	0.511	0.455	0.437	0.487	-
U-N Average	0.454	0.483	0.437	0.420	0.464	0.024

References

1. Rowland, C. E., Kanatzidis, M. G., and Soderholm, L. “Tetraalkylammonium Uranyl Isothiocyantes.” *Inorg. Chem.*, 2012, 51, 11798-11804.