Electronic Supporting Information

Oxidation of uranium(IV) thiocyanate complexes: Cation-cation interactions in mixed valent in uranium coordination chains

Stefano Nuzzo, ^a Jan van Leusen, ^b Brendan Twamley, ^a James A. Platts, ^c Paul Kögerler, ^b and Robert J Baker *^a

a. School of Chemistry, University of Dublin, Trinity College, Dublin 2, Ireland.

b. Institute of Inorganic Chemistry, RWTH Aachen University, D-52074 Aachen, Germany.

c. School of Chemistry, Cardiff University, Park Place, Cardiff, CF10 3AT, UK.

Experimental Procedure

Caution! Natural uranium was used during the experimental work. As well as the radiological hazards, uranium is a toxic metal and care should be taken with all manipulations. Experiments using uranium materials were carried out using pre–set radiological safety precautions in accordance with the local rules of Trinity College Dublin.

All solvents were obtained from commercial sources and used as received. $Cs_4[U(NCS)_8]$ was prepared by the literature method.¹ IR spectra were recorded on a Perkin Elmer Spectrum One spectrometer with attenuated total reflectance (ATR) accessory. Raman spectra were obtained using 785-nm excitation on a Renishaw 1000 micro-Raman system. UV-vis measurements were made on a Perkin Elmer Lambda 1050 spectrophotometer, using fused silica cells with a path length of 1 cm. Steady-state photoluminescence spectra of either solutions or crystalline samples were recorded on a Horiba-Jobin-Yvon Fluorolog-3 spectrofluorimeter in quartz cuvettes with a liquid nitrogen dewar for low temperature measurements. Luminescence lifetime data were recorded following 372-nm excitation, using time-correlated single-photon counting (a PCS900 plug-in PC card for fast photon counting). Lifetimes were obtained by tail fit on the data obtained, and the quality of fit was judged by minimization of reduced chi-squared and residuals squared. Magnetic susceptibility data of 2 were obtained using a Quantum Design MPMS-5XL SQUID magnetometer. The polycrystalline sample was compacted and immobilized into a cylindrical PTFE capsule. DC data were measured as a function of the field (0.1-5.0 T at 2.0 K) and temperature (2.0-290 K at 0.1 T and 1.0 T). AC data were acquired in the absence of a static bias field in the frequency range 1–1000 Hz (T = 2.0-50 K, $B_{ac} = 3$ G), however, no out-ofphase signal was observed. All data were corrected for the diamagnetic contributions of the sample holder and of compound 2 (-1.38×10^{-3} cm³ mol⁻¹).

X-ray structural analyses for crystals of 1 and 2 were performed on a Bruker D8 Quest ECO at 100(2) K with an Oxford Cryosystem cryostat, with samples mounted on a MiTeGen

microloop using Mo K α radiation ($\lambda = 0.71073$ Å). Bruker APEX² software was used to collect and reduce data and determine the space group. Absorption corrections were applied using SADABS.³ Structures were solved with the XT structure solution program⁴ using Intrinsic Phasing and refined with the XL refinement package⁵ using Least Squares minimisation in Olex2.⁶ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to calculated positions using a riding model with appropriately fixed isotropic thermal parameters. Crystallographic data, CCDC 1851382 and 1851383, can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif. Crystal data, details of data collections and refinement are given in Table S1. Polyhedra representations were generated using VESTA version 3.3.9.⁷

Preparation of 1. $Cs_4[U(NCS)_8]$ (70 mg, 0.057 mmol) was dissolved in MeCN (10 cm³) in air and the sample vial covered with parafilm. The solution was left for approx. 1 month by which time emerald green single crystals deposited which were isolated (30 mg, 5.58 x 10⁻³ mmol). All analytical data were measured on these isolated single crystals.

IR (ATR, v/cm⁻¹): 3406 (m, H₂O), 2046 (s, C=N), 1622 (m), 922 (m, U=O), 626 (w, C=S). Raman (v/cm⁻¹): 2129 and 2101 and 2092 and 2076 (C=N), 844 (U=O), 798, 478, 227, 176, 139. UV (ϵ , dm³ mol⁻¹ cm⁻¹), (MeCN, ~ 10⁻⁶ M): 230 nm (74325), 300 (56850). Vis-NIR (ϵ , dm³ mol⁻¹ cm⁻¹), (MeCN, ~ 10⁻³ M): 573 nm (12), 690 nm (52), 925 nm (10), 1074 nm (18), 1406 (24), 1904 nm (115).

Preparation of **2**. $Cs_4[U(NCS)_8]$ (100 mg, 0.081 mmol) was dissolved in DMF (10 cm³) in air and the sample vial covered with parafilm. The solution was left for approx. 1 month by which time emerald green single crystals deposited which were isolated (55 mg, 0.02 mmol). All analytical data were measured on these isolated single crystals.

IR (ATR, v/cm⁻¹): 2933 (w), 2870 (w), 2385 (w), 2046 (s, C=N), 1634 (s), 1485 (m), 1428 (m), 1382 (s), 1245 (m), 1114 (m), 1055 (m), 968 (w), 912 (s, U^{VI}=O), 865 (w, U^V=O), 674 (m, C=S). Raman (v/cm⁻¹): 2558 and 2528 and 2450 (C=N), 1293, 1441, 1423, 1120, 846 (U^{VI}=O), 815 (U^V=O), 710, 671, 503, 404. UV (ϵ , dm³ mol⁻¹ cm⁻¹), (MeCN, ~ 10⁻⁵ M): 302 nm (17121), 344 nm (13381). Vis-NIR (ϵ , dm³ mol⁻¹ cm⁻¹), (MeCN, ~ 10⁻³ M): 503 nm (250), 566 nm (128), 687 nm (536), 858 nm (65), 1159 (320), 1708 (81).

Identification code	1	2
Empirical formula	C112H38C856N112O27S112U16	$C_{56}H_{105}N_{26}O_{19}S_{11}U_4$
Formula weight	18226.70	2751.43
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Instrument	ECO	ECO
Crystal system	Orthorhombic	Monoclinic
Space group	Pna2 ₁	P2 ₁ /n
<i>a</i> (Å)	27.5717(9)	16.7660(7)
<i>b</i> (Å)	27.5456(8)	13.2785(6)
<i>c</i> (Å)	13.5609(5)	44.239(2)
α (°)	90	90
β (°)	90	94.9093(14
γ(°)	90	90
Volume (Å ³)	10299.2(6)	9812.7(7)
Ζ	1	4
ρ (calc. Mg/m ³)	2.939	1.862
μ (mm ⁻¹)	11.764	6.884
F(000)	8054	5276
Crystal size (mm ³)	0.317 x 0.048 x 0.045	0.19 x 0.18 x 0.12
Theta range for data collection (°)	2.336 to 26.126	2.067 to 26.526
Reflections collected	169315	124715
Independent reflections	20437 [R(int) = 0.0543]	20281 [R(int) = 0.0468]
Max. and min. transmission	0.7453 and 0.1322	0.2602 and 0.1626
Data / restraints / parameters	20437 / 51 / 1007	20281 / 0 / 1075
Goodness-of-fit on F ²	1.121	1.229
Final R indices [I>2 σ (I)]	R1 = 0.0290,	R1 = 0.0423,
	wR2 = 0.0558	wR2 = 0.0893
R indices (all data)	R1 = 0.0364,	R1 = 0.0505,
	wR2 = 0.0589	wR2 = 0.0920
Absolute structure parameter	0.423(4)	
Largest diff. peak and hole (e.Å-3)	2.413 and -2.373	2.264 and -2.124
CCDC No.	1851382	1851383

Table S1. Crystal data and refinement details of 1 and 2.

The structure of **1** was refined as an inversion twin with a BASF of 0.423(4) in the noncentrosymmetric SG Pna2₁. Two sulfur atoms on NCS groups are disordered over two locations. S6 (U1, 74:26% occupied) and S12 (U2, 62:38% occupied). Restraints (SADI, SIMU, ISOR) used for convergence. One water molecule is only partially occupied (75%) and is coordinated to Cs5. Water molecule hydrogen atoms were geometrically placed and modelled as riding with a fixed Uiso 1.5 times that of the parent atoms.

In **2**, there are several high residual electron density that could not be assigned to any rational disorder model. They are absorption artefacts that cannot be modelled or eliminated.

Geometry	U1	U3
Spherical capped square	0.665	0.407
antiprism		
Enneagon	36.729	37.282
Octagonal pyramid	22.364	22.036
Heptagonal bipyramid	19.588	19.336
Johnson triangular cupola J3	16.093	16.086
Capped cube J8	10.820	10.755
Spherical-relaxed capped	9.815	9.616
cube		
Capped square antiprism	1.505	1.389
Tricapped trigonal prism	1.947	2.208
Spherical tricapped trigonal	0.584	0.767
prism		
Tridiminished icosahedron	13.055	12.763
J63		
Hula-hoop	12.252	12.186
Muffin	0.990	0.620

 Table S2. Shape analysis for 2. Bold shows the best fit geometry.



Figure S1. Raman (black) and ATR-IR (blue) spectrum 1.



Figure S2. Raman (black) and ATR-IR (blue) spectrum of 2.

	1	2	
	U ^{VI}	U ^{VI}	UV
ν ₁ (U=O)	844	846	815
v ₃ (U=O)	922	912	865
k ₁	6.88	6.83	6.24
k ₁₂	-0.17	-0.08	+0.03



Figure S3. UV-vis/NIR spectrum of **1** in MeCN. UV region (black) measured at 1.10×10^{-6} M solutions and f-f region (red) measured at 1.10×10^{-3} M solutions.



Figure S4. UV-vis/NIR spectrum of **2** in MeCN. UV region (black) measured at 1.19×10^{-5} M solutions and f-f region (red) measured at 1.01×10^{-3} M solutions.



Figure S5. Comparison of the electronic absorption spectra of $[Et_4N]_4[U(NCS)_8]^9$ and **2**. Diagnostic bands due to $[UO_2]^+$ are generally weak and dependent on the geometry of the metal centre,¹⁰ therefore are obscured by the broader more intense f-f transitions of the U(IV) ion.



Figure S6. UV-vis/NIR spectrum of 2 in the solid state.

Further structural description of 1.



Figure S7. Thermal ellipsoid plot of **1** with only metal atoms labelled and bonds to Cs atoms omitted (except coordinated water molecules) for clarity. Displacement shown at 50% probability. The coordination geometry around U1, U2 and U3 are square antiprismatic from Shape analysis (U1: SAPR-8 0.364; U2: SAPR-8 1.180; U3: SAPR-8 0.384).



Figure S8. Packing diagram with U centred polyhedral of **1** viewed normal to the *c*-axis (Colour code:– green polyhedral = U; dark green = Cs; red = O; blue = N; grey = C; yellow = S).



Figure S9. Emission spectrum of 1 in MeCN solution at room temperature ($\lambda_{ex} = 330$ nm, c 1.10 x 10⁻⁶ M).



Figure S10. Emission spectrum of 1 at 77K in solid state ($\lambda_{ex} = 330$ nm).



Figure S11. Excitation spectrum of 1 at 77K in solid state ($\lambda_{em} = 517 \text{ nm}$).



Figure S12. Emission spectrum of 2 in MeCN solution at room temperature ($\lambda_{ex} = 330$ nm; c = 1.19 x 10⁻⁶ M).



Figure S13. Excitation spectrum of **2** at 77K in the solid state ($\lambda_{em} = 514$ nm).

Further Magnetization Data

The lack of divergence in the μ_{eff} vs T plot at different fields rules out the possibility of ferromagnetic impurities. From the shape of μ_{eff} vs T (Fig. 4 in the manuscript), we postulate antiferromagnetic exchange interactions between the uranium centres. The M_m vs B curve (Fig. 4 insert), shows a magnetization of about 0.5 NA μ B at 5 T. Considering that most of the U(IV) compounds have an almost vanishing magnetization at this temperature, the magnetization for three U(IV) centres would be distinctly less than 0.5 NA μ B. In particular (from model calculations using a semi-empirical ligand field approach ("full model"),¹¹ the D_{5h} U(IV) centres are either at almost zero or about 1 NA μ B (for weak ligand fields which is unlikely in this case; we would expect saturation at about 3 T) and the μ_{eff} vs T curve is almost constant with a value of about 3.1 μ B - thus needing rather strong antiferromagnetic exchange interactions to explain the data. Also, antiferromagnetic coupling in an A-B-C-chain tends to give a magnetization value calculated as M(A)-M(B)+M(C) (absolute value of that). Therefore, it is rather unlikely that a single U(IV) centre would fit the data. The D_{5h} U(V) centres show only small shifts of the data, but the curves are in general of same shape $(\mu_{eff}$ vs T almost linear but with a larger slope, M_m vs B as the experimental data). And as a

common feature, their M_m at 5.0 T at 2.0 K is about 0.4-0.5 NA μ B and showing a similar shape as the experimental data.

In the χ_m vs T (Figure S13) plot, the absence of a maximum rules out very strong antiferromagnetic exchange interactions, so they are either small or negligible (consistent with our arguments based on the μ_{eff} vs T and M_m vs B data). However, further points warrant discussion. Firstly, the shape of the curve is similar to μ_{eff} vs 1/T: in particular, there are no shoulders or larger constant values, the latter being characteristic of most U(IV) curves. Secondly, U(V) curves are always like 1/T shaped without such a shoulder. Thirdly, the values of χ_m at 2K and 0.1 T are usually about or less than 0.015 cm³ mol⁻¹ for U(IV), or more than 0.7-0.9 cm³ mol⁻¹ (D_{5h} solution with 3.1 μ_B), whilst for the U(V) compounds, they are all about 0.09 cm³ mol⁻¹. Thus, considering weak antiferromagnetic interactions, the U(IV)-U(V)-U(IV) solution is the most reasonable solution derived from the data.



Figure S14. Plot of χ_m *vs*. T for **2**.

DFT Calculations

All DFT calculations were performed using the ORCA package v 4.0.0.2,¹² using the BP86 functional¹³ and a basis set consisting of 78-electron Lanl2DZ ECP/basis on U and def2-TZVP(-f) on all remaining atoms.¹⁴ Efforts to use small-core 60-electron ECP failed due to SCF convergence issues. All such calculations made use of the resolution of identity method, using ORCA's automatically generated auxiliary basis. Expectation values of the *S*² operator were 3.71, 5.62 and 9.85 for doublet, quartet and sextet states, indicating that some spin contamination is present in these data. AIM analysis used the AIMAII suite,¹⁵ with MultiWfn used as to convert ORCA files to .wfx format.¹⁶
 Table S4. Cartesian coordinates of DFT model of 2

U	10.421100	2.838300	14.598900
U	6.405100	3.271200	15.816100
U	2.527600	3.819800	17.388400
S	14.392800	4.151600	11.518300
S	6.438700	8.371500	14.612100
S	7.960200	5.448200	20.282600
S	7.155600	-0.275100	19.613300
S	5.368400	-1.324800	13.523800
S	4.132800	4.301100	11.238900
0	12.667600	2.887900	15.634600
0	11.873200	1.064500	13.826700
0	9.501800	2.297500	12.450600
0	9.385400	0.593700	14.537400
0	10.378200	1.832500	16.778200
0	10.546600	4.594700	16.209300
0	9.610200	4.907600	13.594200
0	8.186400	3.066900	15.143200
0	4.632900	3.487800	16.525800
0	2.723900	5.865500	16.190700
0	3.989000	5.392000	18.575600
0	3.611200	2.756200	19.235200
0	2.628000	1.455900	16.924100
0	2.263700	3.381400	15.010200
0	0.343600	4.227100	16.518300
0	1.284300	5.226800	18.911900
0	0.880000	2.527500	18.681300
Ν	12.071000	3.794600	13.026700
Ν	14.565600	1.698500	15.942300
Ν	12.413800	-1.025100	13.226400
Ν	8.119200	1.306300	10.957500
Ν	8.716100	-1.418000	15.323600
Ν	10.427200	1.492000	19.015400
Ν	10.150800	6.443000	17.449100
Ν	8.516600	6.264700	12.161700
Ν	6.475600	5.643500	15.233100
Ν	7.282600	4.477800	17.755000
Ν	6.845400	1.660100	17.621600
Ν	5.858400	1.025500	14.936300
Ν	5.541500	3.537100	13.521900
Ν	2.813300	7.464900	14.619100
Ν	5.114000	7.286000	19.090300

Ν	4.904100	2.215600	21.001000
Ν	3.331000	-0.686900	16.812800
Ν	1.996300	2.152700	13.134500
Ν	-1.651300	5.273000	16.499800
Ν	0.576600	6.422700	20.698900
Ν	0.447700	1.191300	20.462400
С	13.041000	3.954700	12.403000
С	13.749200	2.440400	15.231600
Η	14.007400	2.649600	14.341600
С	11.855800	0.127400	13.007300
Η	11.411400	0.262100	12.178600
С	8.391800	1.775200	12.142400
Η	7.719700	1.721800	12.811700
С	8.880100	-0.122600	15.430800
Η	8.598700	0.298200	16.234600
С	10.152800	2.211500	17.950800
Η	9.761200	3.067700	18.077400
С	9.984700	5.698900	16.386700
Η	9.401300	6.016200	15.707400
С	8.643100	5.158300	12.848400
Η	7.956200	4.506300	12.774300
С	6.462400	6.786200	14.963000
С	7.564600	4.888800	18.811100
С	6.982600	0.861000	18.464500
С	5.665000	0.041700	14.352200
С	4.952300	3.855300	12.571600
С	2.867700	6.226000	15.004000
Η	3.025500	5.557900	14.347300
С	4.680900	6.379900	18.243000
Η	4.905900	6.480600	17.325500
С	4.597500	2.974700	19.983200
Η	5.146300	3.728100	19.799400
С	3.455300	0.557800	17.193100
Η	4.220200	0.794000	17.704600
Η	4.087525	-1.423801	17.038736
Η	2.478026	-1.015605	16.237659
С	2.578200	2.415100	14.276500
Η	3.278000	1.841400	14.565600
С	-0.764500	4.497900	17.052000
Η	-0.962500	4.117500	17.899700
С	1.414100	6.176200	19.712000
Η	2.159900	6.754400	19.603100
С	0.860400	2.305800	19.909200
Η	1.167300	2.995600	20.485700

Η	15.441300	1.374100	15.584600
Н	14.341300	1.449700	16.884500
Н	12.831900	-1.244300	14.108000
Н	12.445800	-1.740500	12.528500
Η	8.800000	1.298300	10.225100
Н	7.214400	0.943600	10.734100
Η	9.209700	6.983800	12.211400
Η	7.699400	6.448500	11.615500
Н	8.333500	-1.944600	16.082700
Η	8.940800	-1.913500	14.484600
Η	10.215400	1.839700	19.928800
Η	10.842400	0.584400	18.953100
Η	9.701400	7.332600	17.531100
Η	10.761100	6.196200	18.201900
Η	5.667900	8.063200	18.791900
Η	4.931900	7.227000	20.071800
Η	0.754700	7.151700	21.359800
Η	-0.237300	5.861400	20.849000
Η	-2.524300	5.427500	16.962500
Η	-1.483400	5.763600	15.644700
Η	1.274100	2.738000	12.765900
Η	2.305000	1.390300	12.565700
Η	2.976300	7.727900	13.668200
Η	2.679500	8.207500	15.275400
Η	5.678100	2.441700	21.592400
Η	4.361000	1.414300	21.251800
Η	0.404300	1.062100	21.453100
Η	0.103800	0.433200	19.908300

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