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Well-Defined Molecular Uranium(III) Chloride Complexes

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The first anhydrous, molecular complexes of uranium(III) chloride, soluble in polar aprotic solvents, are reported, including the structures of the dimeric $[UCl_3(py)_4]_2$ and the trimetallic $[UCl(py)_4(\mu\text{-}Cl)_3U(py)_2(\mu\text{-}Cl)_3UCl_2(py)_3]$.

10 The binary salt, UCl_3, was first prepared by Péligot in 1842 *en route* to his landmark isolation of uranium metal.[1] His synthesis required reducing UCl_4 at 500 ºC with dihydrogen. Despite the central importance of transition, main group, and *f*-block metal chlorides as starting materials in inorganic and organometallic 15 synthesis, no simple procedure for the synthesis of a well-defined, anhydrous,[2,3] and polar aprotic solvent soluble UCl_3 starting material has yet been reported. While *in situ* methods for the reduction of UCl_4 to UCl_3 have been developed, the indeterminate nature of the U(III) species and the introduction of 20 by-products that are potentially incompatible with subsequent reactions or efficient work-up have prevented their wide-spread adoption.[4-6] In fact, the recent growth of trivalent uranium chemistry can be directly linked to the ground-breaking, robust methods for the synthesis of well-defined, soluble, molecular 25 UBr_3 and UI_3 complexes, originally developed by Sattelberger and Clark.[7-15]

The development of protocols for the preparation of well-defined UCl_3 precursors provides an alternative halide partner in salt metathesis reactions that produce more readily removed salt 30 by-products, especially when the transmetallation reagents are limited to lithium salts. Additionally, it has been noted that the difficulty in removing alkali metal iodide salts can cause problems in subsequent synthetic procedures due to the propensity of I^- to act as reductant toward uranium(V) and (VI) 35 species.[16] Chloride is also a much more efficient bridging ligand due to its less nephelauxetic character than bromide or iodide. Therefore, UCl_3 precursors may be efficient starting materials for building clusters *via* hydrolysis[17-19] – necessary for modelling uranium waste stream products and biological mediated waste 40 remediation chemistry.[20,21] Most importantly, from a synthetic perspective, uranium metal is not readily available outside the United States. The development of methods to access trivalent uranium from natural abundance or depleted UO_3 (the immediate precursor to UCl_4)[10] allow for the ongoing research efforts of 45 groups outside of the US. Herein, we report straight-forward methods for the synthesis of $[UCl_3(py)_4]_2$ and $[UCl(py)_4(\mu\text{-}Cl)_3U(py)_2(\mu\text{-}Cl)_3UCl_2(py)_3]$.

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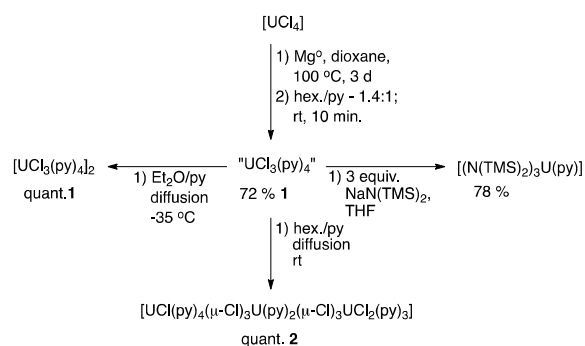
Scheme 1: Synthetic procedures for $[UCl_3(py)_4]_2$ and $[UCl(py)_4(\mu\text{-}Cl)_3U(py)_2(\mu\text{-}Cl)_3UCl_2(py)_3]$.

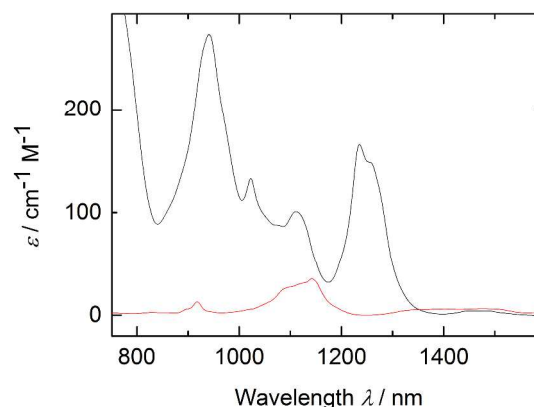**Figure 1:** Absorption spectra of $[UCl_3(py)_4]$, 0.01 M in py (black), and of $[UCl_4]$, 0.01 M in thf (red), $[UCl_4]$ is poorly 55 soluble in py.

The mild reducing conditions employed for the synthesis of $[MoCl_3(THF)_3]$ from $[MoCl_4(THF)_2]$, either with Zn or Sn metal at room temperature,[22,23] suggested that a similar strategy may be 60 applicable for the synthesis of a solvated UCl_3 complex. Initial studies indicated that, while Sn shot led to no reduction of $[UCl_4]$ in 1,4-dioxane at room temperature, Mg metal leads to the gradual (2 weeks) conversion of green $[UCl_4]$ to a blue suspension. For comparison, Kiplinger has recently reported the 65 synthesis of the uranium(IV) dimer $[UCl_4(1,4\text{-dioxane})]_2$ as a yellow/orange powder.[24] Since $[MgCl_2(1,4\text{-dioxane})_2]$ is also

insoluble in 1,4-dioxane, direct identification of the product is not possible, but elemental analysis suggests the formula [UCl$_3$(1,4-dioxane)$_2$]$_2$ • [MgCl$_2$(1,4-dioxane)$_2$]. Identification and purification of the solvated UCl$_3$ was obtained by dissolution in pyridine

5 to give a deep purple solution, followed by fractional crystallization from Et$_2$O/pyridine at –35 °C.

Optimization of this procedure was achieved by heating the 1,4-dioxane suspension of [UCl$_4$] and Mg turnings to 100 °C for 3 days (Scheme 1). The blue suspension can be separated from

10 remaining Mg turnings by decantation onto a glass frit. Dissolution of the blue powder in pyridine (~25 mL per 400 mg of UCl$_4$), followed by filtration to remove a fine, pale green powder (may be the result of ether cleavage or incomplete reduction; however, the identity of this side-product is unknown),

15 and precipitation with 1.4 equivalents of hexane (v/v of pyridine) leads to the isolation of [UCl$_3$(py)$_4$]$_2$, **1**, in 72 % yield as small purple/black crystals (**1** is vacuum sensitive and pyridine incorporation should be confirmed by elemental analysis, box-scale procedure leads to the isolation of **1** in 41 % yield and

20 precisely four equivalents of py per U). A UV/vis/NIR spectrum (Figure 1, black trace) of a 0.01 M solution of **1** clearly indicates trivalent uranium and the absence of tetravalent uranium. The spectrum of **1** is quite similar to that reported for the *in situ* prepared "UCl$_3$(THF)$_x$" in THF.[4] ^{1}H NMR spectroscopy of **1** in

25 pyridine-d_5 with a hexamethylbenzene standard confirms the formula ratio of four pyridines per uranium. However, due to rapid solvent exchange, no peaks associated with bound pyridine can be observed. Most importantly, complex **1** can serve as a synthetic precursor. Hence, the reaction of **1** with 3.0 equivalents

30 of NaN(SiMe$_3$)$_2$ in THF affords the previously reported [U(N(SiMe$_3$)$_2$)$_3$(py)] in 78 % yield.[25]
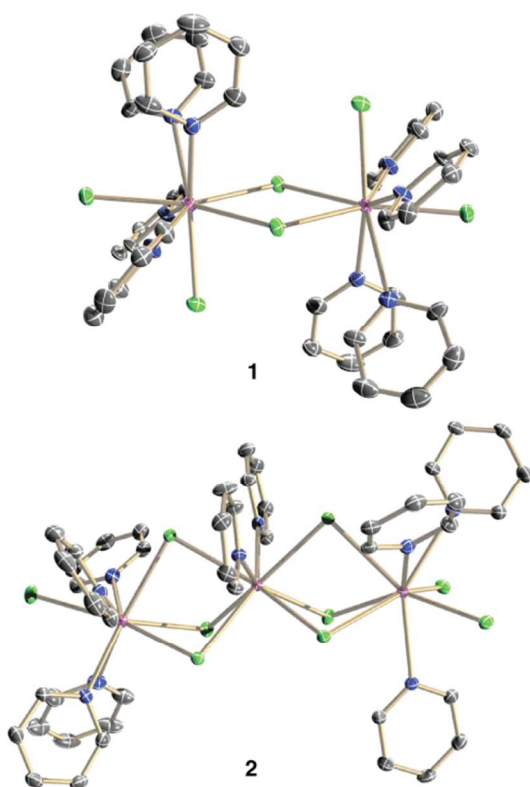
Figure 2: Molecular structures of **1** (in crystals of **1 • 4 C$_5$H$_5$N**) and of **2**. Thermal ellipsoids set at 50% probability. Hydrogen

35 atoms and co-crystalized solvent removed for clarity; U: pink, Cl: green, N: blue, C: dark-grey.

The solid-state molecular structure of **1** was determined by an X-ray diffraction study of crystals **1 • 4 C$_5$H$_5$N** grown by the

40 diffusion of diethyl ether into a pyridine solution of **1** at –35 °C. Crystals prepared in this manner grow as thin layered plates necessitating the acquisition of data on two layers and the solution of the structure as a non-merohedral twin. This solution reveals **1** to be a chloride-bridged dimer in the solid-state with a

45 U$_2$Cl$_2$ diamond core structural motif. The U···U distance is 4.71 Å and U–Cl–U angle is 108.9º. The bridging U–Cl distances are 2.935(2) and 2.853(2) Å (2.936(2) and 2.862(2) Å) (two independently refined UCl$_3$Py$_4$ fragments per asymmetric unit), whereas the terminal U–Cl bond lengths are 2.734(2), 2.759(2),

50 2.740(2), and 2.768(2) Å. The U–N distances span the range from 2.690(8) to 2.772(7) Å.

In an attempt to grow crystals of **1** in another lattice setting, another product, namely [UCl(py)$_4$(μ-Cl)$_3$U(py)$_2$(μ-Cl)$_3$UCl$_2$-(py)$_3$], **2**, was observed in quantitative yield when crystals were

55 prepared by the diffusion of hexane into a dilute solution of **1** in pyridine at room temperature. Notably, to the best of our knowledge, there is no precedent for a trimetallic complex of uranium(III) bridged by a (μ-Cl)$_3$ unit. In complex **2**, the U···U distances are inequivalent at 4.061 Å (U1···U2) and 4.176 Å

60 (U2···U3), respectively. The bridging U–Cl bond distances for U1···U2 are shorter and U1–Cl–U2 angles are contracted in comparison to those for U2···U3. Specifically, the bridging U–Cl bond distance for U1···U2 averages to 2.88 Å and 2.89 Å for U2···U3. Similarly, the U1–Cl–U2 angles span 88.68(2) to

65 90.57(2)º, while the U2–Cl–U3 angles span from 92.19(3) to 92.71(3)º. A similar trimetallic complex of uranium (IV) was presented by Cotton in 1986,[2, 26] namely [(η^6-C$_6$Me$_6$)UCl$_2$(μ-Cl)$_3$UCl$_2$(μ-Cl)$_3$UCl$_2$(η^6-C$_6$Me$_6$)]. The U–Cl bond distances are considerably shorter (2.666(7) to 2.762(6) Å) and the U–Cl–U

70 angles range from 92.4(2) to 93.6(2)º to yield similar U···U distances to those found in **2** (4.035(1) and 4.031(1) Å). However, in comparison to **2**, the central uranium ion is equidistant from the other two uranium ions. The asymmetric bridging (μ-Cl)$_3$ moiety in **2** may be due to the different pyridine

75 binding in U3 and U1 and crystal packing forces. However, the potential for antiferromagnetic coupling to perturb the ground state geometry cannot be discounted.

In conclusion, the first well-defined, molecular complexes of uranium trichloride with practical solubility in common

80 laboratory solvents were prepared and characterized. Reduction of [UCl$_4$] with magnesium turnings affords [UCl$_3$(py)$_4$] readily. Recrystallization from Et$_2$O/pyridine affords the dimeric [UCl$_3$(py)$_4$]$_2$ and recrystallization from hexane/pyridine yields the trimetallic complex, [UCl(py)$_4$(μ-Cl)$_3$U(py)$_2$(μ-Cl)$_3$UCl$_2$(py)$_3$].

85 These compounds should be widely employable reagents for further developments in uranium(III) inorganic coordination and organometallic chemistry. Magnetism studies on the unique trimetallic uranium (III) complex, [UCl(py)$_4$(μ-Cl)$_3$U(py)$_2$(μ-Cl)$_3$UCl$_2$(py)$_3$], **2**, are on-going.

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Notes and references

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1. E.-M. Peligot, *Ann. Chim. Phys.*, 1842, **5**, 5.

2. J. Drożdżyński, *Inorganica Chimica Acta*, 1985, **109**, 79.

15 3. A. Mech, M. Karbowiak, T. Lis and J. Drozdzynski, *Polyhedron*, 2006, **25**, 2083.

4. D. C. Moody and J. D. Odom, *J. Inorg. Nucl. Chem.*, 1979, **41**, 533.

5. R. A. Andersen, *Inorg. Chem.*, 1979, **18**, 1507.

6. J. MacCordick and C. Brun, *Compt. Rend. (C)*, 1970, **270**, 620.

20 7. D. L. Clark, A. P. Sattelberger, S. G. Bott and R. N. Vrtis, *Inorg. Chem.*, 1989, **28**, 1771.

8. L. R. Avens, S. G. Bott, D. L. Clark, A. P. Sattelberger, J. G. Watkin and B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 2248.

9. I. A. Khan and H. S. Ahuja, *Inorg. Synth.*, 1982, **21**, 187.

25 10. J. L. Kiplinger, D. E. Morris, B. L. Scott and C. J. Burns, *Organometallics*, 2002, **21**, 5978.

11. F. G. N. Cloke and P. B. Hitchcock, *J. Am. Chem. Soc.*, 2002, **124**, 9352.

12. W. J. Evans, S. A. Kozimor, J. W. Ziller, A. A. Fagin and M. N.
30   Bochkarev, *Inorg. Chem.*, 2005, **44**, 3993.

13. C. D. Carmichael, N. A. Jones and P. L. Arnold, *Inorg. Chem.*, 2008, **47**, 8577.

14. D. D. Schnaars, G. Wu and T. W. Hayton, *Dalton Trans.*, 2008, 6121.

35 15. L. Natrajan, M. Mazzanti, J. P. Bezombes and J. Pecaut, *Inorg. Chem.*, 2005, **44**, 6115.

16. S. Fortier, J. L. Brown, N. Kaltsoyannis, G. Wu and T. W. Hayton, *Inorg. Chem.*, 2012, **51**, 1625.

17. L. Natrajan, F. Burdet, J. Pecaut and M. Mazzanti, *J. Am. Chem. Soc.*,
40   2006, **128**, 7152.

18. G. Nocton, F. Burdet, J. Pecaut and M. Mazzanti, *Angew. Chem. Int. Ed.*, 2007, **46**, 7574.

19. B. Biswas, V. Mougel, J. Pecaut and M. Mazzanti, *Angew. Chem. Int. Ed.*, 2011, **50**, 5744.

45 20. Y. Suzuki, S. D. Kelly, K. M. Kemner and J. F. Banfield, *Nature*, 2002, **419**, 134.

21. B. H. Gu, H. Yan, P. Zhou, D. B. Watson, M. Park and J. Istok, *Environ. Sci. Technol.*, 2005, **39**, 5268.

22. J. R. Dilworth and J. Zubieta, *Inorg. Synth.*, 1986, **24**, 193.

50 23. J. R. Dilworth and R. L. Richards, *Inorg. Synth.*, 1980, **20**, 121.

24. M. J. Monreal, R. K. Thomson, T. Cantat, N. E. Travia, B. L. Scott and J. L. Kiplinger, *Organometallics*, 2011, **30**, 2031.

25. J. L. Stewart, Ph.D. Thesis, 1988, University of California, Berkeley, CA.

55 26. G. C. Campbell, F. A. Cotton, J. F. Haw and W. Schwotzer, *Organometallics*, 1986, **5**, 274.

$[UO_3] \longrightarrow [UCl_4] \longrightarrow [UCl_3(py)_4]_2$

Graphical Abstract: