Easy access to stable pentavalent uranyl complexes†

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Reaction of $UO_2I_2(THF)_3$ with 1 molar equivalent of KC_5R_5 (R = H, Me) in pyridine led to the uranyl(V) compound $\{[UO_2(Py)_5][KI_2(Py)_2]\}_\infty$, which is an infinite 1D polymer in its crystalline form; the $UO_2X(THF)_n$ (X = I, OSO_2CF_3) complexes were obtained by reduction of their U(VI) parents with TlC_5H_5 or KC_5R_5 in THF.

Uranyl(VI) compounds have been extensively studied, but little is known about their reduced forms containing the pentavalent $\{UO_2\}^+$ ion, which is quite unstable towards disproportionation, leading to U^{4+} and $\{UO_2\}^{2+}$ derivatives. The synthesis of isolable complexes of the $\{UO_2\}^+$ ion would permit crucial insights to be gained into its physicochemical properties in relation to theoretical analysis,[1] and allow comparisons to be made with the more stable $\{AnO_2\}^+$ ions (An = Np, Pu, Am)[2] that play a major role in both the nuclear industry and the natural environment.

While studies on UO_2X_2 species (X = halide, OSO_2CF_3, NO_3, ClO_4, *etc.*) in aqueous solutions have afforded limited information on their chemical behaviour, significant recent advances were possible by the use of strictly anhydrous conditions.[3–6] In particular, the electrochemically generated $[U^VO_2(DBM)(DMSO)]^-$ and $[U^VO_2(Saloph)(DMSO)]^-$ species (DBM = dibenzoylmethanate, Saloph = *N,N′*-disalicylidene-*ortho*-phenylenediaminate) proved to be quite stable in DMSO[5] but were not isolated. The sole uranyl(V) compound to have been crystallographically characterized, $[UO_2(OPPh_3)_4][OSO_2CF_3]$, was obtained fortuitously during the crystallisation of its U(VI) parent from a mixture of acetonitrile and diethyl ether.[6] However, the reproducible synthesis and isolation of stable $\{UO_2\}^+$ species remain highly desirable. We found that the reduction of UO_2I_2 and $UO_2(OTf)_2$ (OTf = OSO_2CF_3) with cyclopentadienyl anions or potassium amalgam in THF or pyridine constitutes a convenient route to pentavalent uranyl complexes. Here we report on the synthesis and characterization of the compounds $UO_2X(THF)_n$ (X = I, OTf) and $\{[UO_2(Py)_5][KI_2(Py)_2]\}_\infty$; the crystal structure of the latter having been determined.‡

Reaction of $UO_2I_2(THF)_3$ with 1 molar equivalent of KC_5H_5 or KC_5Me_5 in pyridine reproducibly led to an orange suspension that was stable for many days at 20 °C. Thin orange needles of $\{[UO_2(Py)_5][KI_2(Py)_2]\}_\infty$ (**1**) suitable for X-ray diffraction analysis were deposited in a few hours when a 1 : 1 mixture of $UO_2I_2(THF)_3$ and KC_5Me_5 was heated in pyridine and then cooled down to room temperature.§ The bright orange product obtained by filtration of the suspension was dried under vacuum to give an ochre powder, the elemental analyses of which (C, H, N, I) corresponded to the formula $UO_2(Py)_{2.2}I_2K$ (**2**) (eqn. 1) (80% yield). Slow diffusion of diethyl ether into a pyridine solution of **2** afforded crystals of **1**. An orange powder was also formed when uranyl iodide was reacted with K(Hg) in pyridine, but separation of the product from the residual mercury was difficult.

$$\begin{tikzcd}
UO_2I_2(THF)_3 + KC_5R_5 \arrow[r, "\text{Pyridine}", "- C_5R_5^{\bullet}"'] & \{[UO_2(Py)_5][KI_2(Py)_2]\}_\infty \ \mathbf{(1)} \arrow[d, "\text{Vacuum drying}"'] \\
 & UO_2(Py)_{2.2}I_2K \ \mathbf{(2)}
\end{tikzcd} \qquad (1)$$

A view of **1** is shown in Fig. 1, together with selected bond distances and angles.¶ The structure consists of *trans* dioxo linear $\{UO_2\}^+$ cations, surrounded in the equatorial plane by five pyridine ligands, and linked by the oxo groups with $\{KI_2(Py)_2\}$ anionic fragments. The U=O bond lengths of 1.843(2) and 1.842(2) Å are slightly larger than those measured in the hexacoordinate mononuclear complex $[UO_2(OPPh_3)_4]^+$ (1.817(6) and 1.821(6) Å),[6] but are shorter than those determined by EXAFS studies in the anion $[UO_2(CO_3)_3]^{5-}$ (1.90(2) Å).[8] They are also similar to those found in the mono-oxo organometallic U(V) compound $U(C_5Me_5)_2(=O)(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (1.859(6) Å)[9] and the

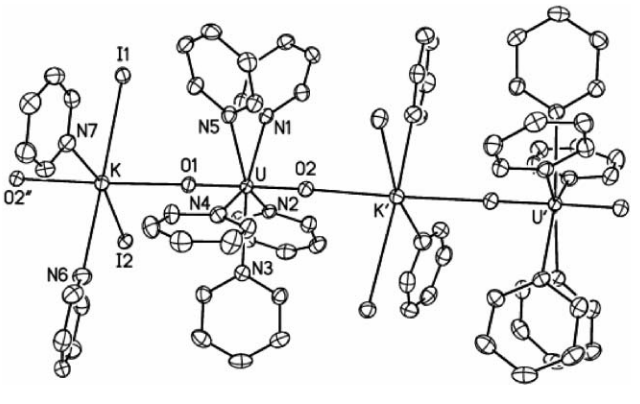

Fig. 1 View of the 1D polymer $\{[UO_2(Py)_5][KI_2(Py)_2]\}_\infty$ (**1**). The H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): U–O1 1.8431(19), U–O2 1.8415(19), U–N1 2.612(3), U–N2 2.590(3), U–N3 2.605(3), U–N4 2.593(3), U–N5 2.597(3), K–O1 2.798(2), K′–O2 2.811(2), K–N6 3.195(3), K–N7 2.891(3), K–I1 3.5355(7), K–I2 3.5229(7); O1–U–O2 178.85(9), K–O1–U 178.63(11), U–O2–K′ 175.62(11). Symmetry codes: ′ x − 0.5, 1.5 − y, z − 0.5; ″ x + 0.5, 1.5 − y, z + 0.5.

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mixed-valent U(V/VI) oxo-imido dimeric anion $[UO(\mu_2\text{-}NCH_2CH_2N(CH_2CH_2NSi^tBuMe_2)_2)]_2^-$ (1.838(5) Å).[4c]

The mean U–N distance of 2.599(8) Å is slightly larger than in the neutral U(VI) compounds $UO_2I_2(Py)_3$ (2.54(3) Å),[3b] $UO_2(OTf)_2(Py)_3$ (2.53(2) Å)[3c] and $UO_2(\eta^2\text{-}NO_3)_2(Py)_2$ (2.543(15) Å),[10] but is identical to that found in $UO_2(^tBuCOCHCOMe)_2(Py)$ (2.595(24) Å).[11] The two groups of atoms U, N1, N2, N3, N4, N5 and K, I1, I2, N6, N7 define two planes (rms deviations 0.052 and 0.139 Å, respectively), which are almost parallel, with a dihedral angle of 4.28(7)°. The K–O distances of 2.798(2) and 2.811(2) Å can be compared with that of 2.757(5) Å found in the complex $[UO_2K(LH_3)(H_2O)_2]_2$ (LH_6 = *para*-*tert*-butylhexahomotrioxacalix[6]arene).[12c]

The polymeric structure of **1**, which forms an infinite chain, is ensured by cation–cation interactions. These are now well documented in uranyl(VI) and neptunyl(V) chemistry,[12,13] and reflect the pronounced Lewis basicity of the axial oxygen atoms of the $\{UO_2\}^+$ moiety, which is related to the nature and number of the equatorial ligands. Greater basicity of the $\{UO_2\}^+$ ion with respect to that of its $\{UO_2\}^{2+}$ analogue is expected, in line with the lower positive charge on the metal centre and consequently the greater electron density on the oxygen atoms.

The preparation of soluble $UO_2X(L)_n$ compounds (L = THF, Py), which would be useful starting materials for the further development of uranyl(V) chemistry, is of special interest. Treatment of $UO_2I_2(THF)_3$ with a 1 molar equivalent of TlC_5H_5 afforded, after the usual work-up,§ a brown solid in 73% yield, which was determined to be $UO_2(THF)_{2.7}I$ (**3**) (eqn. 2). Compound **3** proved stable in pyridine and, when heated in this solvent in the presence of excess KI, gave orange needles of complex **1** within a few hours of cooling to room temperature.

$$UO_2I_2(THF)_3 + TlC_5H_5 \xrightarrow[-\,C_5H_5^{\bullet}]{THF} \underset{\mathbf{(3)}}{UO_2I(THF)_{2.7}} + TlI \tag{2}$$

The formation of **3** indicated that other halides or pseudo halides of the $\{UO_2\}^+$ ion, which are generally more stable than the iodide congener, should be isolable. Indeed, similar treatment of uranyl(VI) triflate with KC_5R_5 (R = H, Me) led to the formation of a beige powder, the elemental analysis of which was found to vary with vacuum drying, and correspond to the formula $UO_2(OTf)(THF)_n$ (**4**) where *n* = 1.5 and 2 (eqn. 3). The yield was 84%.§ The low number of coordinating ligands after desolvation, as observed in compounds **2** and **3**, suggests the formation of oligomeric species with iodide or triflate bridges. Attempts to obtain crystals suitable for X-ray diffraction analysis by recrystallizing **3** and **4** from various organic solvents in which they are perfectly stable (THF, pyridine, acetonitrile), in the presence or absence of added organic ligands, have so far been unsuccessful. However, here again, addition of excess KI into a pyridine solution of **4** led to a brown-orange solution, from which orange needles of **1** were deposited after several days, thus confirming the formation of an U(V) complex.

$$UO_2(OTf)_2 + KC_5R_5 \xrightarrow[-\,C_5R_5^{\bullet}]{THF} \underset{\substack{\mathbf{(4)}\\(n\,=\,1.5\text{–}2)}}{UO_2(OTf)(THF)_n} + KOTf \tag{3}$$

The infrared spectra in Nujol mulls show strong absorption bands assigned to the UO_2 stretching vibration mode at 797, 847 and 853 cm^{-1} for **2**, **3** and **4**, respectively. These values are larger than that of the 770 cm^{-1} reported for the pentavalent $[UO_2(Saloph)(DMSO)]^-$ anion.[5c] By comparison with the corresponding U(VI) parents $UO_2(OTf)_2$ (982 cm^{-1}), $UO_2(OTf)_2(THF)_3$ (964 cm^{-1}), $UO_2(OTf)_2(Py)_3$ (943 cm^{-1}),[3c] $UO_2I_2(Py)_3$ (927 cm^{-1}) and $UO_2I_2(THF)_3$ (928 cm^{-1}),[3b] these wave numbers are reduced by *ca.* 100–180 cm^{-1}, in agreement with the longer $U^V{=}O$ bonds. These differences are close to that reported for the analogous uranyl(VI)- and uranyl(V)-saloph complexes (125 cm^{-1}).

In conclusion, reactions of uranyl(VI) iodide and triflate with cyclopentadienyl anions lead to the formation of uranyl(V) compounds, which represent potential precursors for further developments in U(V) chemistry. Characterization of stable pentavalent uranyl complexes, with different coordination environments around the $\{UO_2\}^+$ ion, indicate that such species should be isolable from various organic media and not only, as generally thought, with a restricted choice of proper equatorial ligands.

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Notes and references

‡ The synthesis and crystal structure of complex **1** were reported after submission of this communication.[7] Mazzanti *et al.* prepared this compound in 54% yield by following a distinct route *via* the oxidation of $UI_3(THF)_4$ with pyridine oxide in the presence of water, followed by addition of potassium iodide.

§ *Synthesis and characterizing data.* **Compounds 1 and 2**: A flask was charged with $UO_2I_2(THF)_3$ (250 mg, 0.33 mmol) and KC_5Me_5 (59 mg, 0.33), and pyridine (15 mL) was condensed in. After stirring for 2 h at 20 °C, THF (5 mL) was added and the orange powder filtered off. Drying under vacuum gave a beige powder of **2** (200 mg, 80%). Found: C, 18.03; H, 1.48; N, 4.24; I, 34.66. $C_{11}H_{11}I_2KN_{2.2}O_2U$ requires C, 17.93; H, 1.50; N, 4.34; I, 34.44%. Slow diffusion of diethyl ether into a pyridine solution of **2** gave crystals of **1** (*ca.* 50% yield). **Compound 3**: A flask was charged with $UO_2I_2(THF)_3$ (298 mg, 0.40 mmol) and freshly sublimed TlC_5H_5 (111 mg, 0.41 mmol), and THF (15 mL) was condensed in. After stirring for 6 h at 20 °C, the brown solution was filtered and concentrated to 5 mL. The brown powder, which precipitated upon addition of pentane (15 mL), was filtered off and dried under vacuum (175 mg, 73%). Found: C, 21.91; H, 3.46; I, 20.95. $C_{11}H_{22}IO_{4.75}U$ requires C, 22.20; H, 3.72; I, 21.32%. **Compound 4**: A flask was charged with $UO_2(OTf)_2$ (300 mg, 0.53 mmol) and KC_5Me_5 (92 mg, 0.53 mmol), and THF (20 mL) was condensed in. The suspension was stirred for 15 h at 20 °C, and after extraction with a mixture of THF (10 mL) and toluene (15 mL), evaporation of the solvents led to a brown powder, which was recrystallized from THF–pentane (5–20 mL). The beige powder was filtered off and dried under vacuum for 15 h at room temperature (233 mg, 84%). The elemental analyses correspond to the formula $UO_2(OTf)(THF)_{1.5}$. Found: C, 16.32; H, 2.14; F, 10.44. $C_7H_{12}F_3O_{6.5}SU$ requires C, 15.95; H, 2.29; F, 10.81%. By following the same procedure with $UO_2(OTf)_2$ (306 mg, 0.54 mmol) and KC_5H_5 (58 mg, 0.55 mmol), the beige powder was dried for 10 h at 20 °C (220 mg, 72%). The elemental analyses correspond to the formula $UO_2(OTf)(THF)_2$. Found: C, 19.03; H, 2.43; F, 9.88. $C_9H_{16}F_3O_7SU$ requires C, 19.19; H, 2.86; F, 10.12%.

¶ *Crystal data for* $\{[UO_2(Py)_5][KI_2(Py)_2]\}_\infty$ (**1**): $C_{35}H_{35}I_2KN_7O_2U$, M = 1116.63, monoclinic, space group $P2_1/n$, a = 12.8453(4), b = 19.1818(7), c = 16.0316(5) Å, β = 100.794(2)°, V = 3880.2(2) Å^3, Z = 4, D_c = 1.911 g cm^{-3}, μ = 5.921 mm^{-1}, $F(000)$ = 2108, T = 100(2) K, 126670 measured reflections, 7370 independent (R_{int} = 0.024), 6271 with $I > 2\sigma(I)$, 433 parameters, R_1 = 0.021, wR_2 = 0.041. The data were collected on a Nonius Kappa-CCD diffractometer with Mo-Kα radiation. Absorption effects were empirically corrected. CCDC 605512. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605710a

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