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Catalytic one-electron reduction of uranyl(vi) to Group 1 uranyl(v) complexes via Al(III) coordination†

Markus Zegke, Gary S. Nichol, Polly L. Arnold* and Jason B. Love*

Reactions between the uranyl(vi) Pacman complex [(UO$_2$)(py)(H$_2$L)] of the Schiff-base polypyrrolic macrocycle L and Tebbe’s reagent or DIBAL result in the first selective reductive functionalisation of the uranyl oxo by Al to form [(py)(R$_2$AlOOUO)(py)(H$_2$L)] (R = Me or Bu). The clean displacement of the oxo-coordinated Al(III) by Group 1 cations has enabled the development of a one-pot, DIBAL-catalysed reduction of the U(vi) uranyl complexes to a series of new, mono-oxo alkali-metal-functionalised uranyl(v) complexes [(py)$_2$(MOOUO)(py)(H$_2$L)] (M = Li, Na, K).

The uranyl(vi) dication UO$_2^{2+}$ is the most common form of uranium in the environment, and is reduced by minerals and microbes to the less stable uranyl(v) monocation UO$_2^+$, the chemistry of which has only recently been investigated in detail.1–4 The [Rn] 5f$^1$-electron configuration of uranyl(v) results in a variety of interesting properties such as cation–cation interactions (CCIs)5 and single molecule magnetism (SMM),6 and provides insight into often non-trivial 5f-electron behaviours.7 Exploring the uranyl(v) oxidation state may help in understanding the fundamental uranium-based processes occurring in groundwater remediation and nuclear fuel corrosion.8 Furthermore, due to the increased Lewis basicity of UO$_2^+$ compared to UO$_2^{2+}$,8 uranyl(v) complexes may also be employed to model the behaviour of highly radioactive neptunyl ions NpO$_2^{2+}$ which are present in nuclear waste.10 Studies by us11 and others12,13 on the reactions of uranyl(vi) complexes with silyl-containing reagents have led to new reductive oxo-functionalisation reactions being uncovered, forming stable silylated uranyl(v) complexes and a chemically inert and air-stable butterfly-shaped bimetallic uranium(v) dioxo complex.14 As with reductive metalation reactions of the uranyl(vi) dication, the stability of uranyl(v) complexes against disproportionation is dramatically enhanced through the functionalisation of the more Lewis-basic oxo group of this $f^1$ cation.15,16 Here, we report synthetic routes to the first oxo-aluminated uranyl(v) complexes, transmetalation reactions to the first mono-alkali metal uranyl(v) adducts supported by the Pacman ligand, and a new procedure to alkali-metal functionalised uranyl(v) complexes that is catalytic in the Al(III) reagent. Significantly, these complexes are exclusively exo-oxo metalated, and show high stability against disproportionation to uranyl(vi) and uranium(iv) compounds.17,18

We have studied a range of Al(III) compounds that might behave as suitable electrophiles to the accessible oxo group of the uranyl ion in the uranyl(vi) Pacman complex [(UO$_2$)(py)(H$_2$L)] A.19 In particular, two compounds [Cp$_2$Ti(m-Cl)(m-CH$_2$)AlMe$_2$] (Tebbe’s reagent) and [(Bu)$_2$AlH]$_2$ (DIBAL) have proven to be excellent sources of the oxophilic and Lewis acidic Al(III) cation (Scheme 1).

The combination of benzene solutions of equimolar quantities of A and [Cp$_2$Ti(m-Cl)(m-CH$_2$)AlMe$_2$], followed by the addition of 0.1 mL of pyridine at room temperature results in a clear orange solution from which yellow crystals form upon standing, characterised as [(py)Me$_2$AlOOUO(py)(H$_2$L)] 1, and isolated in 67% yield. The X-ray crystal structure of 1 was determined and shows the expected wedge-shaped Pacman geometry of the parent complex with exo-oxo aluminium coordination (Fig. 1). The uranyl oxo groups adopt a trans geometry, with an O1–U1–O2 angle of 174.3(1)$^\circ$ and U1–O1 and U1–O2 bond lengths elongated to 1.857(3) $\AA$ and 1.962(3) $\AA$ respectively, compared to the O–U–O bonds of

![Scheme 1 Reductive alumination of [(UO$_2$)(py)(H$_2$L)], A by Tebbe’s reagent or DIBAL.](image-url)
1.793(6) Å and 1.773(6) Å for A. This significant lengthening of these bonds is indicative of a decrease in the uranyl bond order and is similar to related experimental and calculated systems in which an increase of 0.151–0.242 Å in U–O bond lengths upon reduction of O–UO=c=c=O to O–UO=O–O–M is seen. Furthermore, the hydrogen-bonding interactions between the endo-oxo O1 and the two pyrrole protons in the vacant macrocyclic pocket, shown by O1···N1 2.964(5) Å and O1···N2 3.068(5) Å are slightly shorter than those in A (3.111(7) Å and 3.146(7) Å) and supports the enhanced oxo basicity of the f² cation. To our knowledge, this is the first reaction in which Tebbe’s reagent is used as a source of aluminium.

A more atom-economic route to these heterobimetallic complexes is through the reaction between A and DIBAL in toluene at 70 °C for 24 h which results in the formation of yellow [(py)(tBu2AlO)(py)(H2L)]2 in 51% yield. The solid state structure of 2 (Fig. 1) is very similar to 1, once more exemplifying the formal U⁷ oxidation state through an elongation of the U1–O1 and U1–O2 bond distances. Mechanistically, it is likely that 1 and 2 are formed through Al–ligand bond homolysis (Al–H or Al–C) which provides the reducing electron. This process is similar to that suggested by us previously to be responsible for U⁷ reduction in the formation of lithium-functionalised [Li(UO)(py)(Li)] and lanthanide-functionalised [UO2(py)(Li)]₂ that result from Li–C or Ln–N bond homolysis.

The 1H-NMR spectrum of 2 (see ESI†) shows contact-shifted and broadened resonances between -6 and +70 ppm due to the paramagnetism of the f² centre. Even so, the tBu methyl hydrogens can be identified at 6.10 ppm and 6.67 ppm with JH–H coupling of 8 Hz, and the methine proton is a broad resonance at 11.31 ppm that couples with the methylene protons at 16.35 ppm and 16.81 ppm. The most contact-shifted resonance at +69 ppm is assigned to the pyrrole N–H protons. In situ measurements show the formation of gaseous H₂ at 4.49 ppm. Both UO₂-Al⁺⁺ compounds 1 and 2 are stable in THF and pyridine solvents. A study of the redox chemistry of 2 by cyclic voltammetry in THF with 0.1 M [NBu₄][PF₆] as a supporting electrolyte at 500 mV s⁻¹ reveals a quasi-reversible reduction at E₁/₂ = -1.42 V (vs. Fe/Fc) which is tentatively ascribed to a uranyl(V)/uranium(IV) redox couple (see ESI†). A pre-reduction wave is also seen at Epc = -1.45 V, implying that the redox chemistry of 1 and 2 is not straightforward, and as yet, in line with related U(V) complexes that we have studied, the chemical reduction of complex 1 or 2 has not yet been successful. However, we have found that the AlR₂ group is readily substituted by Group 1 metal cations by reaction with an alkyl or hydride reagent such as MeLi, NaH or KH (Scheme 2); these experiments had been anticipated to deprotonate the two, likely acidic, pyrrole NHs in 1 and 2.

Reactions between benzene solutions of 1 with either one or two equivalents of the strong base MeLi affords solely [{OUO-Li(py)(H₂L)}₂] in moderate isolated yield (40%), which remains U⁷ and doubly NH protonated. This contrasts with the reactions of the uranyl(V) Paeman complex [UO₂(py)(H₂L)] with single equivalents of LiR (R = H, NH₂, NPr₂, N(SiMe₃)₂, CPh₃, C₅H₅) which simply result in pyrrole deprotonation to afford the uranyl(V) complex [{UO₂(py)(LiHL)}₂] and suggests that the hydrogen-bonding interaction between the f² uranyl oxo group and the pyrrole protons is significant enough to attenuate deprotonation. The X-ray crystal structure of 3 (Fig. 2) shows that the lithium cation is coordinated by the imine groups of the macrocycle and that the uranium centre has migrated from its usual N₄ donor pocket to an alternative pyrrole–imine–imine–pyrrole disposition. The Li cation is thus sited within the cavity of the macrocycle, bound to the uranyl endo-oxo atom, the two imine groups, and a molecule of pyridine. As in the other complexes the
uranil is five-coordinate in the equatorial plane but the site which was occupied by the donor solvent is now filled by the exo-oxo group of its counterpart in the dimer, resulting in a diamond-shaped UO3–
cation–cation interaction.1,2,16 The uranium–uranium separation in
complex [(py)3(LiOUO)(py)(Li(py)2L)]26 was verified by 1H-NMR spectroscopy and crystal structure
analysis (unit cell check). In contrast, reactions between 1 or 2
and an excess of LiH in the donor solvent pyridine at 40 °C
results in the formation of the known, triply lithiated, uranyl(v)
complex [(py)3(LiOUO)(py)([Li(py)]2)L].27 The difference in ability of the two types of Li reagents (LiR
or LiH) to effect N–H deprotonation is likely due to the nature of
the reaction solvent. The use of pyridine stabilises the exogenous
coordination of a Li cation for the respective alkali metal to yield
[(py)3(NaOUO)(py)(H2L)].27

The difference in ability of the two types of Li reagents (LiR vs.
LiH) to effect N–H deprotonation is likely due to the nature of
the reaction solvent. The use of pyridine stabilises the exogenous
coordination of the Li cation to the uranyl oxo group, whereas in
benzene, the reorganization of the uranyl coordination pocket allows
for maximum interaction of the Li cation with the macrocycle. In
support of this, the addition of pyridine to a benzene solution of
3 shows a rearrangement from the bowl-shaped structure to 4, possessing
the classical Pacman Ca22n.3,3,3

Fig. 2 Solid-state structure of 3. For clarity, all hydrogen atoms except
pyrrole NH and all solvent molecules are omitted (displacement ellipsoids are
drawn at 50% probability). Selected bond lengths (Å) and angles (°): U1–O1 1.908(2), U1–O2 1.891(2), U1–O1’ 2.372(3), N4–O2 3.269(4), N7–O2 3.198(5). O1–U1–O2 177.7(1), U1···U1’: 3.5199(9). as such, reactions that incorporate DIBAL are significantly accelerated.

The solid state structures of 4, 5 and 6 (side view). For clarity, all
hydrogen atoms except pyrrole N Hs and all solvent molecules are omitted
(displacement ellipsoids are drawn at 50% probability). Selected bond lengths (Å)
and angles (°) for 4: U1–O1 1.8536(6), U1–O2 1.8847(7), O1–N4 3.091(1), O1–N5 3.1001(6), O1–U1–O2 173.8(3), O1–U1–O1’ 1.844(5), U1–O2 1.856(7), O1–N4 3.010(9), O1–N5 2.998(8), O1–U1–O2 174.23(3), 6: U1–O1 1.872(2), U1–O2 1.837(2), O1–N4 2.898(4), O1–N5 2.932(4), O1–U1–O2 176.1(1). only one resonance at 88.48 ppm, supporting Li coordination to the

The solid state structures of 4, 5 and 6 are very similar, and
in contrast to 3 show the classic uranyl Pacman geometry. The
main difference between the structures is that the U1–O2–M1
angle is nearly linear for the Li (4) (173.8(3)) and Na (5) (174.7(6))
complexes whereas the U1–O2–K1 angle is considerably
bent (116.0(1)). This is caused by an η1-interaction between K
and a U-bound pyrrolide ring due to the softness and size of K+ (152 pm)
compared to Na+ (112 pm) and Li+ (73 pm).28

It is clear from the above transmetalation reactions that the
aluminium by-product is the alane or aluminium hydride. As
such it was envisaged that formation of the reduced, alkali-
metallated uranyl complexes 4–6 from A should be achievable
using MH (M = Li, Na, K) and a catalytic amount of AlH(iBu)2, as
this latter reagent should be regenerated during the trans-
metalation step. As such, reactions using 10 mol% of DIBAL
and an excess of MH in toluene at 70 °C for 72 to 96 hours
(Scheme 2) were carried out and are found to generate 4, 5 or 6
in essentially quantitative yields (Table 1, showing reactions
using KH only). Control reactions with no aluminium reagent
formed 50% of 6 after 96 hours, and increasing the reaction
time up to ten days afforded a 4:1 mixture of 6 and A; as such,
reactions that incorporate DIBAL are significantly accelerated.

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Table 1  Example conditions for the HA[i-Bu]2-catalysed reduction of UO22+ with KH

<table>
<thead>
<tr>
<th>Entry</th>
<th>mol% HA[i-Bu]2</th>
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<th>Ratio 6/A</th>
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</tr>
<tr>
<td>5</td>
<td>0</td>
<td>240</td>
<td>80/20</td>
</tr>
</tbody>
</table>

Reactions conditions: 70 °C, toluene, 5 equivalents KH.

Treatment of A with 5 mol% of DIBAL only gave 20% of 6 with 80% of the starting material still present, even after a prolonged reaction time.

Additionally the redox chemistry of 6 was studied by cyclic voltammetry in THF with 0.2 M [NBu4][PF6] as a supporting electrolyte at scan rates between 100 and 500 mV s⁻¹ and reveals a quasi-reversible reduction at E₁/₂ = −1.31 V (vs. Fe/Fe⁺) which is ascribed to a uranyl(v)/uranyl(VI) redox couple (see ESI†).

We report the first reductive alumination of the uranyl dication which results in a significant attenuation of the acidity of the pyrrole NHs through hydrogen bonding to the f⁰ centre, such that reactions with Group 1 bases result in transmetalation instead of the deprotonation chemistry previously seen. This change in reactivity has allowed us to develop a new synthetic route to simple, catalytic in aluminium reagent. This new Al-mediated route should provide opportunities for new catalysed uranyl functionalisation reactions with other d- and f-group metal cations, and could even offer a general low-cost, one-pot route to the selective Group 1 cation metathesis of d-block metal oxo complexes.

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Notes and references


