

Pentavalent uranyl stabilized by a dianionic bulky tetradentate ligand†

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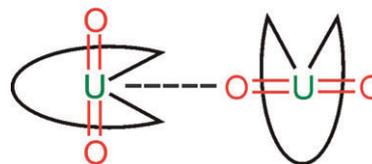
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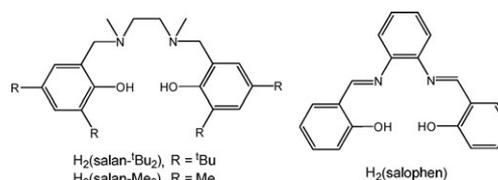
A pentavalent uranyl complex supported by a bulky dianionic tetradentate (ONNO)-type salan ligand has been prepared by direct synthesis from the iodide precursor $\{[\text{UO}_2\text{Py}_5][\text{KI}_2\text{Py}_2]\}_n$, and displays high stability towards disproportionation and ligand dissociation but reactivity towards oxidizing substrates.

Besides its high fundamental interest, the chemistry of pentavalent uranyl has important environmental implications.^{1–3} Furthermore, the preparation of stable pentavalent uranyl complexes is crucial for reactivity studies and for the development of uranyl-based photocatalysts.⁴ UO_2^{2+} is highly unstable in solution and, except in low pH or concentrated aqueous carbonate solutions,⁵ it readily disproportionates to form U(IV) and UO_2^{2+} .¹ Uranyl(V) complexes including the Schiff base complex $[\text{UO}_2(\text{salophen})(\text{dmsO})]^-$ ($\text{H}_2(\text{salophen}) = N,N'$ -phenylene-bis(3,5-di-*tert*-butylsalicylideneimine) have been first produced in anhydrous dmsO by electrochemical reduction of the UO_2^{2+} analogue, but never isolated using this route.⁶ Only recently, a few complexes of pentavalent uranyl have been isolated in the solid state from anhydrous organic solutions and structurally characterized.^{7–11} However most of these complexes undergo disproportionation often accompanied by ligand displacement in solution (with partial decomposition occurring in the time range 2–24 h).^{8,11} In one case, the disproportionation reaction was demonstrated to involve the formation of a dimeric complex (Scheme 1) through the mutual binding of two uranyl(V) groups (commonly known as cation–cation interaction, CCI).¹¹ Apart from the solution-stable complex $\{[\text{UO}_2\text{Py}_5][\text{KI}_2\text{Py}_2]\}_n$ (**1**),⁷ Arnold and co-workers prepared the only other known solution-stable pentavalent uranyl by using a bulky macrocyclic ligand in the presence of a transition metal cation.⁹ Notably, the preparation of solution-stable but reactive complexes remains a challenge in the development of UO_2^{2+} chemistry.

Here we report the first pentavalent uranyl complex supported by a diamine bis-phenolate salan ligand.‡ The tetradentate ligand $\text{salan-}^t\text{Bu}_2^{2-}$ ($\text{H}_2(\text{salan-}^t\text{Bu}_2) = N,N'$ -bis(2-



Scheme 1



Scheme 2

hydroxybenzyl-3,5-di-*tert*-butyl-1,2-dimethylaminomethane) (Scheme 2) contains anionic donor atoms capable of tight binding in the equatorial plane of the uranyl moiety and provides the bulk necessary to prevent disproportionation through cation–cation interactions (CCIs). While salen ligands have been often employed in uranyl(VI) chemistry,¹² the use of salan ligands, which are versatile and easy to synthesize, has only been limited to lanthanide and d-block metal chemistry.¹³

Most of the previously reported uranyl(V) species have been obtained by the reduction of a hexavalent precursor. However, this strategy requires a careful choice of the reducing conditions. Therefore the use of the iodide complex of U(V) $\{[\text{UO}_2\text{Py}_5][\text{KI}_2\text{Py}_2]\}_n$ (**1**)⁷ as a starting material provides a very convenient route to the preparation of UO_2^{2+} complexes. Notably, this synthetic method allows a rapid assessment of the stabilizing effect of the chosen ligand with respect to the disproportionation reaction. It should be noted that the reaction of **1** with $\text{K}_2(\text{salophen})$ in pyridine leads to a mixture of U(IV), U(V) and U(VI) species.¹⁴ Conversely, the reaction of **1** with $\text{K}_2(\text{salan-}^t\text{Bu}_2)$ in pyridine solution (Scheme 3) leads to the formation of a complex of pentavalent uranyl, which crystallizes in a polymeric form $[\text{UO}_2(\text{salan-}^t\text{Bu}_2)(\text{py})\text{K}]_n$ (**2**) and is highly stable with respect to the disproportionation reaction.

For comparison the hexavalent complex $[\text{UO}_2(\text{salan-}^t\text{Bu}_2)(\text{py})]$ (**3**) was prepared from the reaction of $\text{H}_2(\text{salan-}^t\text{Bu}_2)$ with uranyl nitrate in pyridine and both were crystallographically characterized. The molecular structure of **2** and **3**, elucidated by X-ray diffraction,§ confirms the presence of UO_2^{2+} and UO_2^{2+} cations, respectively. ORTEP views of **3** and of **2** are shown in Fig. 1.

In both complexes the uranium atom is seven-coordinated with a regular pentagonal bipyramidal coordination geometry.

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† Electronic supplementary information (ESI) available: Synthetic details, crystallographic details for compounds **2** and **3**, visible, NMR and IR spectra. CCDC reference numbers 711672 and 711673. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b821398d

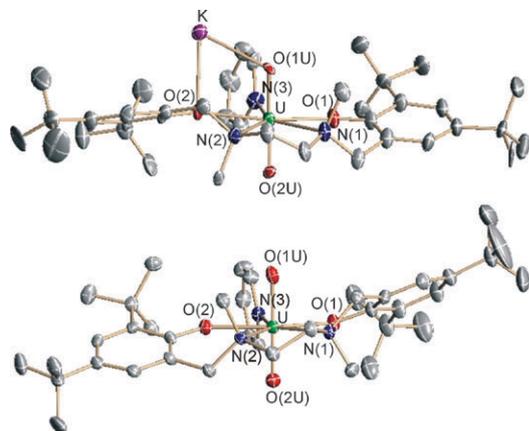
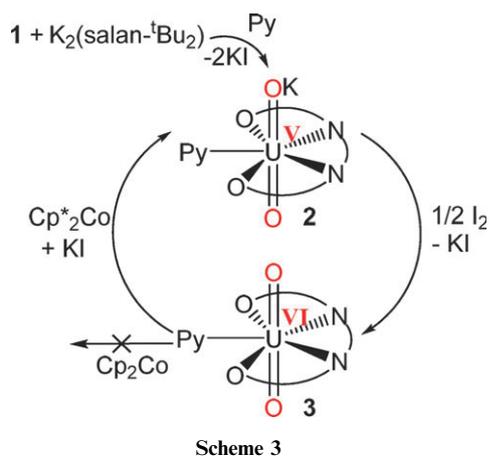


Fig. 1 ORTEP view of **2** (top) and of **3** (bottom) with thermal ellipsoids at the 30% probability level. Hydrogen atoms and solvent molecules were omitted for clarity. Selected bond lengths (Å) and angles (°) for **2**: U–O1U 1.819(12), U–O2U 1.830(12), O1U–U–O2U 178.9(6); for **3**: U–O1U 1.764(4), U–O2U 1.790(3), O1U–U–O2U 178.37(18).

The four donor atoms of the *salan*-*t*Bu₂²⁻ (O₂N₂) and the pyridine nitrogen form a pentagonal plane (a mean deviation of 0.07 Å in **2** and of 0.04 Å in **3**). The ligand wraps around the metal with the two methyl groups in a *trans* position taking a chiral pseudo-*C*₂ symmetry. The axial positions are occupied by two oxo ligands. In **2**, both oxo groups are involved in a CCI with the potassium ion (mean K–O distance of 2.68(2) Å), linking uranium complexes along the *c* axis into a 1-D chain (U···K···U angle of 123.7°) (Fig. S7, ESI†). The potassium ion also coordinates the phenolate oxygen of the *salan*-*t*Bu₂ (K–O 2.697(1) Å). A similar 1-D polymeric arrangement was found in the structure of **17** but with longer K–O distances (2.84(7) Å) and a larger U···K···U angle (178.2°). This results in a smaller separation between neighboring U(v) ions in **2** (6.63 Å) as compared to **1** (9.35 Å). The presence of a pentavalent uranyl leads to a significant elongation of the U–*salan*-*t*Bu₂ distances (0.14 Å for U–O) and of the U=O(oxo) bond lengths (0.05 Å) with respect to complex **3**, as observed in other structurally characterized UO₂⁺ and UO₂²⁺ complexes.^{7,8} In the IR spectra the UO₂ asymmetric stretching frequency is shifted to a lower value for the U(v) complex **2** (750 cm⁻¹) compared to its U(vi) analogue

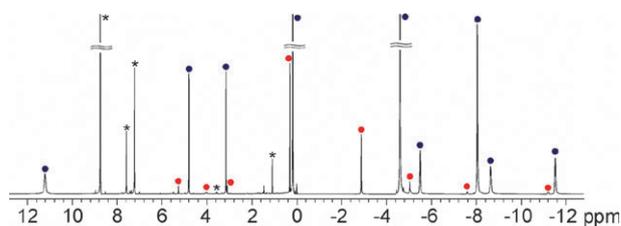


Fig. 2 ¹H NMR spectrum of **2** in pyridine-*d*₅ at 298 K (unchanged after 4 weeks). Red and blue dots indicate the minor *C*_s and major *C*₂ isomers, respectively, asterisks indicate solvents.

3 (873 cm⁻¹) in agreement with the presence of a longer U=O bond distance. Similar values (895 and 770 cm⁻¹, respectively, for UO₂⁺ and UO₂²⁺) were reported for the [UO₂(*salphen*)(*dms*o)]^{0/-} complexes.⁶ The rigid coordination of the *salan*-*t*Bu₂²⁻ ligand to the metal centre leads to the presence of different isomers in solution. The major set of signals in the ¹H NMR spectrum in pyridine solutions of **2** (Fig. 2) and **3** was assigned to monomeric rigid *C*₂-chiral (racemic) solution species consistent with the ligand conformation in the solid state structure. Minor *C*_s symmetric species are also present in solution for both complexes (5.7% for **2** and 19.0% for **3**). The NMR spectrum of **2** shows a paramagnetic shift of the signals in agreement with the presence of the UO₂⁺ ion. The effective magnetic moment measured in pyridine solution ($\mu_{\text{eff}} = 2.35 \mu_{\text{B}}$) is smaller than the value predicted for the free U(v) ion ($\mu_{\text{eff}} = 2.54 \mu_{\text{B}}$) but similar to those found for other mononuclear U(v) compounds.¹⁵ The uranyl(v) complex **2** is highly stable in solution and no decomposition is observed for up to one month in pyridine, and *dms*o. Even the presence of stoichiometric amounts of water does not lead to the disproportionation of complex **2**, but to the slow ligand loss as the only observed decomposition pathway (Fig. S14, ESI†). These results show that the bulky dianionic *salan*-*t*Bu₂²⁻ ligand provides a very effective protection of the UO₂⁺ group disfavoring the formation of oxo-bridged intermediates (UO₂⁺–UO₂⁺ cation–cation complexes shown in Scheme 1) and therefore preventing disproportionation. The importance of the steric profile of the *tert*-butyl groups in preventing disproportionation was confirmed by the reaction of **1** with the dianionic *salan*-Me₂²⁻ (*salan*-Me₂H₂ = *N,N'*-bis(2-hydroxybenzyl)-3,5-dimethyl)-1,2-dimethylaminomethane) ligand in pyridine. The reaction leads to the formation of a UO₂⁺ complex of *salan*-Me₂ which rapidly disproportionates to U(IV) and to UO₂²⁺ species.

Preliminary studies show that complex **2** reacts rapidly with various oxidizing agents. Light pink solutions of **2** in pyridine are readily oxidized by O₂, I₂ or CH₂Cl₂ producing red solutions of the hexavalent analogue. NMR studies show that the reduction of the resulting U(vi) complex with Cp*₂Co ($E_{1/2\text{CH}_2\text{Cl}_2} = -1.94 \text{ V vs. Fc/Fc}^+$)¹⁶ in pyridine restores the stable U(v) complex of *salan*-*t*Bu₂ (Scheme 3). No traces of a disproportionation reaction were observed during the oxidation–reduction cycle. Conversely, the U(vi) complex is not reduced by the weaker reducing agent Cp₂Co ($E_{1/2\text{CH}_2\text{Cl}_2} = -1.33 \text{ V vs. Fc/Fc}^+$)¹⁶ in pyridine. These results position the redox potential of **2** ($E_{1/2}(\text{UO}_2^+/\text{UO}_2^{2+})$) between –1.94 and –1.33 V in agreement with the value found for

$[\text{UO}_2(\text{salophen})(\text{dmsO})]^- E_{1/2\text{dmsO}}(\text{UO}_2^+/\text{UO}_2^{2+}) = -1.55 \text{ V}$ vs. Fc/Fc^+). The UO_2^+ complex of $\text{salan-}^t\text{Bu}_2^{2-}$ can also be obtained by reduction of **3** with Cp^*Co in pyridine (Fig. S11, ESI†). The resulting complex is also stable in pyridine solution with respect to disproportionation, indicating that the bulky salan ligand can stabilize the uranyl(v) moiety even in the absence of cations coordinated to the uranyl oxygen.

In conclusion, amine phenolate ligands have been used to prepare a uranyl(v) complex. The ligand $\text{salan-}^t\text{Bu}_2^{2-}$ leads to the stabilization of UO_2^+ with respect to the disproportionation reaction. The versatility of these ligands, for which the geometry and the electronic properties can be finely tuned by the replacement of the aliphatic spacer and of the ring substituents,¹³ opens new perspectives for the development of the chemistry of pentavalent actinyls. Future work will involve the design of ligands leading to increased stability in water. Furthermore, the easy conversion by oxidation/reduction between UO_2^+ and UO_2^{2+} renders this compound particularly suitable for reactivity studies and lays the basis for the potential development of uranium-based oxidation catalysts. Work in both directions is in progress.

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Notes and references

† Synthesis of $[\text{UO}_2(\text{salan-}^t\text{Bu}_2)(\text{Py})\mu\text{K}]_n$ (**2**). A solution of $\text{K}_2(\text{salan-}^t\text{Bu}_2)$ (141.6 mg, 0.236 mmol) in pyridine (1.5 mL) was added to a suspension of **1** (263.1 mg, 0.236 mmol) in pyridine (1.5 mL) resulting within minutes in a clear dark pink/orange solution, which was stirred for 1 hour. The solvent was concentrated under vacuum to a volume of 0.5 mL. A dark pink precipitate, obtained after addition of $^i\text{Pr}_2\text{O}$ (10 mL), was subsequently filtered, washed 3 times with $^i\text{Pr}_2\text{O}$ (3 mL) and dried under vacuum. Yield: 170 mg (58%) Anal. calcd for $[\text{UO}_2(\text{salan-}^t\text{Bu}_2)(\text{Py})\mu\text{K}]_n \cdot 2\text{KI} \cdot \text{C}_{39}\text{H}_{59}\text{UN}_3\text{O}_4\text{K}_3$: C, 37.68; H, 4.78; N, 3.38. Found: C, 37.54; H, 5.10; N, 3.38. ^1H NMR (pyridine- d_5 ; 298 K; 400 MHz, 12.62 mM) δ in ppm: two sets of signals correspond to C_2 (major) and C_3 (minor) isomers (presented in Fig. 2) in the ratio 100 : 5.7. C_2 (major isomer): -11.25 (br, 2H, -NCH₂-); -8.25 (br, 2H, -NCH₂-); -7.91 (s, 6H, -N(CH₃-)); -5.21 (br, 2H, -NCH₂-Ph); -4.49 (s, 18H, -^tBu); 0.15 (s, 18H, -^tBu); 3.23 (s, 2H, -CH_{aromatic}); 4.84 (s, 2H, -CH_{aromatic}); 11.65 (br, 2H, -NCH₂-Ph). C_3 (minor isomer): -11.00 (br, 2H, -NCH₂-); -7.44 (br, 2H, -NCH₂-Ph) -5.01 (br, 2H, -NCH₂-); -4.84 (s, 3H, -N(CH₃-)); -2.80 (s, 18H, -^tBu); 0.29 (s, 18H, -^tBu); 3.06 (s, 2H, -CH_{aromatic}); 5.29 (s, 2H, -CH_{aromatic}).

§ Crystal data for complex **2**: $\text{C}_{40.5}\text{H}_{62.5}\text{KN}_3\text{O}_4\text{U}$, $M = 932.57$, monoclinic, $a = 11.7846(3)$, $b = 30.2442(5)$, $c = 13.0298(3)$ Å,

$\beta = 102.368(2)$, $V = 4536.26(17)$ Å³, $T = 100(1)$ K, space group $P2_1/c$, $Z = 4$, $D_c = 1.365$ g cm⁻³. Synchrotron radiation with $\lambda = 0.69408$ Å and MAR345 detector were used for data collection (SNBL at the ESRF). $F(000) = 1878$, 12 949 were reflections, 3824 unique ($R_{\text{int}} = 0.0446$), R (on F) = 0.0641, wR (on F^2) = 0.1726 ($I > 2\sigma I$).

3: $\text{C}_{40.5}\text{H}_{62.5}\text{KN}_3\text{O}_4\text{U}$, $M = 893.47$, monoclinic, $a = 19.6726(6)$, $b = 20.0780(6)$, $c = 11.4096(3)$ Å, $\beta = 101.116(3)$, $V = 4422.1(2)$ Å³, $T = 150(2)$ K, space group $P2_1/c$, $Z = 4$, $D_c = 1.342$ g cm⁻³, $F(000) = 1802$, 25 664 reflections measured, 9620 unique ($R_{\text{int}} = 0.0464$), R (on F) = 0.0403, wR (on F^2) = 0.0690 ($I > 2\sigma I$).

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