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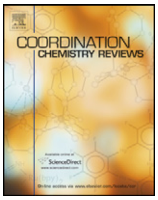

Review

Pentavalent uranyl complexes

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Contents

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ABSTRACT

The uranyl dication, $[UO_2]^{2+}$, is the most prevalent and most thermodynamically stable form of uranium and is a soluble and problematic environmental contaminant. It is also extraordinarily chemically robust due to the strongly covalent *trans*-UO_2 bonding. In contrast, the pentavalent uranyl cation $[UO_2]^+$ is unstable in an aqueous environment with respect to disproportionation into tetravalent uranium species and $[UO_2]^{2+}$. Aside from fundamental interest, an understanding of the pentavalent $[UO_2]^+$ cation is desirable since it is important environmentally as a key intermediate in the precipitation of uranium from groundwater.

In the last 2 years, the use of anaerobic coordination chemistry techniques and organometallic reagents has allowed the isolation of a few kinetically inert complexes containing the f^1 $[UO_2]^+$ cation. The synthesis and characterisation of these, and the insight they give into subsequent reactivity of the *trans*-UO_2 unit, is discussed in this review.

1. Introduction

1.1. The actinyl $[AnO_2]^{n+}$ cations

The majority of high oxidation state complexes of the actinides contain the actinyl ions, $[AnO_2]^{n+}$ (where An = U, Np, Pu; $n = 1$ or 2). In contrast to the transition metal dioxo complexes that almost always adopt bent geometries [1], the actinyl ions are essentially linear. Uranium is the only one of these three actinides to occur naturally in the environment, and, as the least radioactive of the three, the uranyl dication is the most widely studied and potentially important linear metal dioxo cation. The chemistry of uranium is dominated by the dioxo or uranyl dication, $[UO_2]^{2+}$, which is found both in aqueous solutions and in the solid state. To date the Cambridge Structural Database contains over 2000 single crystal X-ray structures of uranium compounds, over half of which contain the uranyl dication [2]. It should be mentioned that recently a coordination polymer containing a *cis*-uranyl dication, $[UO_2(Fcdc)(thf)\text{-}(Fc)]_n$ (Fcdc = 1,2-ferrocenedicarboxylate, Fc = ferrocene) was reported as the product of the reaction of uranyl acetate with ferrocene dicarboxylate [3], but this assignment has since been called into question [4].

The U—O bonds are particularly thermodynamically strong and kinetically inert due to the overlap of a combination of metal 5f and 6d, and oxygen 2p orbitals to produce one σ and two π bonds with a formal triple U—O bond order [5–7]. The generation of these hybrid orbitals at uranium for axial oxo bonding leaves few orbitals

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Abbreviations: acac, acetylacetonate; CCI, cation–cation interaction; Cp, C_5H_5; Cp*, C_5Me_5; dbm, dibenzoylmethanate; DMF, dimethylformamide; DMSO, dimethylsulphoxide; Fc, ferrocene, $Fe(\eta^5\text{-}C_5H_5)_2$; hfac, $CF_3C(O)CHC(O)CF_3$; NMR, nuclear magnetic resonance; OTf, O_3SCF_3; py, pyridine; THF, tetrahydrofuran.

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with which to bind all other ligands at the uranium centre. Almost without exception, these remaining ligands bind in the equatorial plane perpendicular to the O═U═O axis [8,9].

Unlike the uranyl dication, many transition metal oxo complexes exhibit extensive Lewis base chemistry and are involved in a variety of catalytic and stoichiometric reactions such as hydrocarbon oxidation [8], oxygen atom transfer [9] and cycloaddition reactions [1,10,11].

The most closely related d-block species to the actinyl ions is the osmyl ion, $[OsO_2]^{2+}$, which is also linear. In spite of the difference in the ionic radii of the metal ions (U^{VI} = 0.73 Å, Os^{VI} = 0.545 Å), the U–O bond length of ca. 1.80 Å is close to that of the Os–O double bond of ca. 1.75 Å [12]. In contrast, the $[MoO_2]^{2+}$ dication which is in the same group as $[UO_2]^{2+}$ but contains no accessible *f*-orbitals, is bent.

The *f*-electrons in actinides display varying localised or band structural behaviour across the series. This gives rise to solid-state compounds with exotic magnetic properties including heavy Fermion states, non-Fermi liquid behaviour, unconventional superconductivity, and magneto-optical effects [13–18]. For theoretical methods to describe accurately and predict these properties, they need to account for *f*-electron (de)localisation, strong spin–orbit interactions, strong electron correlations, crystal electric field effects, phonon effects, and hybridization between *f* orbitals and conduction states [19,20]. Since U^V has the simplest 5*f* electron configuration $[Rn]5f^1$, these f^1 systems are useful for magnetic and spectroscopic studies through which we can better understand the *f*-electron behaviour [21].

1.2. Behaviour of the uranyl dication in the environment

The actinyl ions are highly soluble in water, and therefore mobile in the environment. This mobility of the $[UO_2]^{2+}$ dication contributes to concerns about the long-term underground storage of nuclear waste [22], and in uranium mining operations [23]. Recent years have seen a renewed interest in the redox behaviour of uranium species in relation to the environmental fate of uranium and the transport and treatment of mixed-waste [24,25]. In an anaerobic environment, the U^{VI} ion will be reduced to U^{IV} minerals such as uraninite which are water-insoluble, so uranium is effectively immobilised at this point [26]. Also, the uranyl ion can undergo bacterial anaerobic reduction from U^{VI} to the insoluble U^{IV} species, offering a strategy for the bioremediation of uranium-containing groundwater [27,28]. Experimental work on heterogeneous systems, also in an anaerobic environment (and in the absence of carbonate ion), has shown that uranyl is heterogeneously reduced by sulfides, and a range of Fe^{II}-containing minerals such as micas, magnetite, and annite [29]. Experiments on solutions of uranyl in contact with nanocrystalline magnetite have shown fast kinetics for uranium sorption and reduction at the surface, with an overall long-term loss in uranium from solution as it is precipitated [30]. Magnetite is the most important end member of iron corrosion products under reducing environment, which is the condition expected in a deep geological high level radioactive waste disposal.

The reduction of $[UO_2]^{2+}$ to U^{IV} phases is thought to proceed *via* single electron transfer to form pentavalent uranyl, $[UO_2]^+$. Unlike neptunyl and plutonyl, which are stable in multiple oxidation states [31] uranium is only briefly stable as $[UO_2]^+$, and in aqueous conditions is known to readily disproportionate to form tetravalent uranium species and $[UO_2]^{2+}$ (Eq. (1)), with the low charge on the ion precluding the formation of complexes that are stable towards disproportionation [32].

$$2[UO_2]^+ + 4H^+ \rightarrow U^{4+} + [UO_2]^{2+} + 2H_2O \qquad (1)$$

Due to this instability and inertness, the knowledge of the chemistry of pentavalent uranyl is very limited [33–35]. However, recent advances in non-aqueous, air-sensitive chemistry have lead to the discovery of some non-classical uranyl chemistry such as the isolation of a number of pentavalent uranyl complexes, which are the focus of this paper.

It should be noted that although not as common as the tetravalent and hexavalent states, many non-yl complexes of U^V have been reported [33,36–38], but are outside the scope of this review.

2. Pentavalent uranyl complexes

2.1. In situ syntheses of $[UO_2]^+$ complexes

Millimolar solutions of $[UO_2]^+$ can be obtained by electrolytic reduction of $[UO_2]^{2+}$, reduction of $[UO_2]^{2+}$ with zinc amalgam or dihydrogen, dissolution of UCl_5, or by combining solutions of some U^{IV} and U^{VI} solutions, although electrolytic reduction is the preferred method [33].

The electrochemical reduction of $[UO_2]^{2+}$ complexes in anaerobic solutions affords pentavalent uranyl complexes such as compounds **1**–**3** (Fig. 1) [39,40]. Ligands such as the tetradentate Schiff-base phenoxide 'salophen', and more commonly, a variety of β-diketonate ligands are bound in the equatorial plane to stabilise the singly reduced uranyl cation. The disproportionation of the $[UO_2]^+$ ion is sufficiently slow in an aqueous environment between pH 2 and 4 to allow solutions to be spectroscopically characterized, but these compounds are generally studied in DMF solution with $Bu_4{}^nN(ClO_4)$ as supporting electrolyte [29,41]; they have not yet been isolated free from electrolyte solution, or independently synthesised [42–44]. The U^{VI}/U^V redox waves measured are generally reversible or quasi-reversible.

Photo-activated uranyl ions are much more reactive than ground state uranyl ions. In oxygen-free water, the photochemical reaction between uranyl and sucrose forms $[UO_2]^+$ which disproportionates thermally to U^{IV} and U^{VI} states [45]. Organic compounds such as alcohols can be photo-oxidised in the presence of $[UO_2]^{2+}$ [46].

2.2. Discrete $[UO_2]^+$ complexes

The first report of a pentavalent uranyl complex characterised in the solid state was in 2003 by Berthet et al. [47]. In their studies on the synthesis of anhydrous uranyl triflate compounds, crystals of $[UO_2(OPPh_3)_4][OTf]$, **4**, were obtained serendipitously from the crystallisation of $[UO_2(OPPh_3)_4][OTf]_2$. The crystals of **4** contain dis-

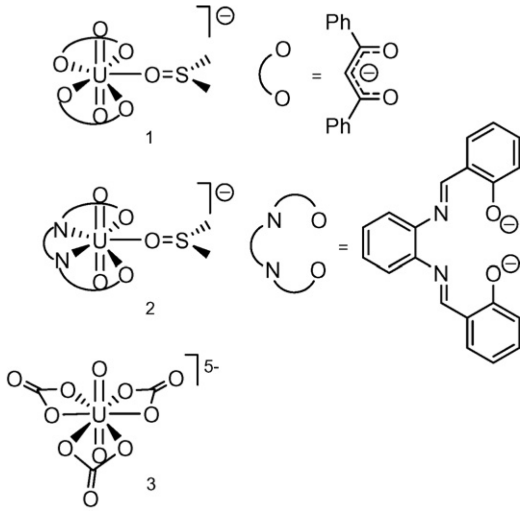
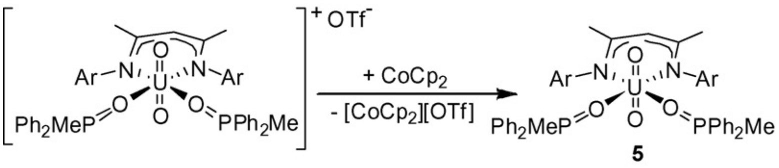


Fig. 1. $[UO_2]^+$ complexes produced by electrochemical reduction methods.



Scheme 1. Synthesis of $[UO_2(Ar_2nacnac)(Ph_2MePO)_2]$, **5** ($Ar = 2,6\text{-}^iPr_2C_6H_3$).

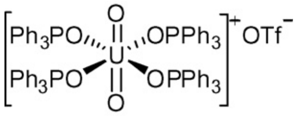


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Fig. 2. The complex $[UO_2(OPPh_3)_4][OTf]$.

crete cation–anion pairs, and the uranyl-containing cation displays an octahedral geometry with a linear uranyl (Fig. 2).

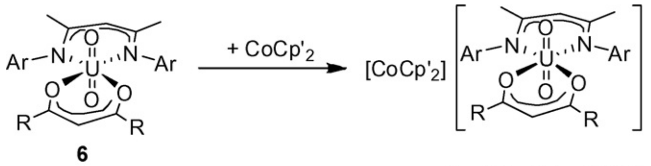
The U═O distances of 1.817(6) and 1.821(6) Å correspond to a lengthening of the uranyl-oxo bond by 0.06 Å compared to the hexavalent analogue, $[UO_2(OPPh_3)_4)]^{2+}$ (1.76(1) Å). The U═O bond lengths in **4** are longer than those reported for the analogous Np═O bond lengths (1.797(2) Å) in the isostructural $[NpO_2(OPPh_3)_4]^+$ ion [48], and this concurs with the differences between the radii of $[UO_2]^+$ and $[NpO_2]^+$ ions (ionic radii of 6-coordinate $U^V = 0.76$ Å, $Np^V = 0.75$ Å) [49,50]. It was also reported that the average U-$OPPh_3$ bond distance (2.44(2) Å) was much longer (by 0.14 Å) than those in the analogous hexavalent complex, a feature arising from the decrease in positive charge at the U^V centre. Attempts were made to reproduce the synthesis of **4**, including UV-photolysis of $[UO_2(OPPh_3)_4)]^{2+}$ and treatment with various chemical reductants, but all these routes proved inconclusive. Although this discovery of a stable pentavalent uranyl complex was a breakthrough, the difficulty of accessing this compound encouraged a quest to synthesise other stable $[UO_2]^+$ complexes with reproducible syntheses.

Hayton and Wu isolated a pentavalent uranyl complex **5** by reduction of a hexavalent uranyl complex stabilised by a careful choice of equatorial ligands (Scheme 1) [51]. The bulky $[Ar_2nacnac]^-$ ligand anion ($[Ar_2nacnac]^- = [(2,6\text{-}^iPr_2C_6H_3)NC(Me)CHC(Me)N(2,6\text{-}^iPr_2C_6H_3)]^-$; $Ar = 2,6\text{-}^iPr_2C_6H_3$) stabilises the pentavalent uranyl product by providing steric bulk in the uranyl equatorial plane and along the O═U═O axis. This bulk also prevents the formation of cation–cation complexes (see below) which are proposed to initiate disproportionation reactions [52]. The hexavalent complexes $[UO_2(Ar_2nacnac)(DPPMO_2)][OTf]$ ($DPPMO_2 = Ph_2P(O)CH_2P(O)Ph_2$) and $[UO_2(Ar_2nacnac)(Ph_2MePO)_2][OTf]$ were shown to undergo a one electron electrochemical reduction by cyclic voltammetry at −1.14 V and −1.45 V (vs. Fc/Fc^+), respectively. However, chemical reduction of $[UO_2(Ar_2nacnac)(DPPMO_2)][OTf]$ with cobaltocene (Cp_2Co) results in the loss of $H^{\bullet}$ from the usually robust phosphine backbone of the $DPPMO_2$ ligand. In contrast, the chemical reduction of $[UO_2(Ar_2nacnac)(Ph_2MePO)_2][OTf]$ with Cp_2Co resulted in the formation of the desired pentavalent uranyl complex $[UO_2(Ar_2nacnac)(Ph_2MePO)_2]$, **5**.

Complex **5** was characterized in the solid state by X-ray diffraction, and has a distorted octahedral geometry with a linear uranyl group (178.4(2)°). The uranium-oxo bond lengths of 1.810(4) and 1.828 (4) Å are similar to those for the other pentavalent complexes reported above and are longer than those seen in the hexavalent precursor (1.756(4) and 1.748(4) Å). The asymmetric uranyl stretch for **5** was observed at 800 cm^{-1}, and corresponds to a decrease of 118 cm^{-1} compared to that of the hexavalent precursor, indicating that the bonding within the pentavalent uranyl fragment is weakened. Complex **5** was also characterised in solution by NMR spectroscopy and UV–vis spectroscopy. The ^1H and $^{31}P\{^1H\}$ NMR spectra of **5** support the formation of a paramagnetic compound and no remaining resonance in the $^{19}F\{^1H\}$ NMR spectrum. The UV–vis spectrum of **5** has an absorption at 755 nm ($\varepsilon = 56\ mol^{-1}\ dm^3\ cm^{-1}$), consistent with an *f*–*f* transition; the energy and intensity of this transition are similar to those reported for the pentavalent species characterised by Ikeda and co-workers in 2.1 [43]. Even though it is isolable, **5** exhibits partial decomposition after 24 h in solution, with complete decomposition observed after 1 week. The only identifiable decomposition products are those of the free ligands $H(Ar_2nacnac)$ and Ph_2MePO, and the fate of the uranium remains unknown.

By replacement of the phosphine oxide ligand with different β-diketonate ligands, it is possible to tune the reduction potential of the uranyl dication. The incorporation of electron-withdrawing substituents at the R position of the β-diketonate ligand makes the reduction of the hexavalent uranyl complexes easier. For example, the reduction potential of $[UO_2(Ar_2nacnac)(RC(O)CHC(O)R)]$ ($Ar = 2,6\text{-}^iPr_2C_6H_3$) **6** is −1.82 V (R = Me), −1.59 V (R = Ph), and −1.30 V ($R = CF_3$) (vs. Fc/Fc^+) as measured by cyclic voltammetry. These readily accessible reduction potentials allow the chemical reduction of the complexes with either $CoCp^*_2$ or $CoCp_2$ in toluene and results in the formation of the complexes $[CoCp^*_2][UO_2(Ar_2nacnac)(acac)]$ (R = Me) **7**, $[CoCp^*_2][UO_2(Ar_2nacnac)(dbm)]$ (R = Ph) **8**, and $[Cp_2Co][UO_2(Ar_2nacnac)(hfac)]$ ($R = CF_3$), **9** (Scheme 2).

The solid-state structure of **8** consists of discrete cation/anion pairs and the uranium metal centre has a distorted octahedral geometry with a linear $[UO_2]^+$ group (179.9(6)°). Due to the low quality of the crystallographic data, confident comparisons of the bond lengths between the hexavalent and pentavalent uranyl complexes could not be made. However, the U–O(dbm) and U—N bond lengths in **8** are longer than those in the hexavalent precursor in line with the larger $[UO_2]^+$ ion. The ^1H NMR spectrum of **7** in CD_2Cl_2 displayed broad and upfield-shifted resonances that support the presence of the paramagnetic uranyl(V) ion, while the $^{19}F\{^1H\}$ NMR spectrum of **9** in CD_2Cl_2 displayed a broad singlet at −10.1 ppm. The UV–vis spectra for complexes **7**–**9** contain absorptions that are consistent with *f*–*f* transitions and the presence of a $5f^1$ ion. Complex **7** has absorptions at 791 nm ($\varepsilon = 75\ mol^{-1}\ dm^3\ cm^{-1}$) and 844 (210), **8** at 743 (170) and 634 (220) and **9** at 677 (430). The solid-state IR spectra displayed uranyl asymmetric stretches at 838 (**7**), 844



R = Me, Cp′ = Cp*, **7**
R = Ph, Cp′ = Cp*, **8**
R = CF_3, Cp′ = Cp, **9**

Scheme 2. The synthesis of pentavalent uranyl complexes **7**, **8** and **9** ($Ar = 2,6\text{-}^iPr_2C_6H_3$).

(**8**), and 864 cm^{-1} (**9**); these values correspond to a shift to lower frequency between 58 and 95 cm^{-1} compared to that of the hexavalent starting materials. All three reduced complexes were found to be air- and water-sensitive, decomposing upon standing in air within 24 h at room temperature, with the only identifiable product of decomposition the $H(Ar_2nacnac)$ ligand.

Interestingly, reduction of $[UO_2(Ar_2nacnac)(acac)]$ **6** (R = Me) with sodium in THF followed by cation exchange with $[NEt_4]Cl$ resulted in the isolation of $[NEt_4][UO_2(Ar_2nacnac)(H_2C{=}C(O)CH(O)CMe)]$ as red crystals in 17% yield, which is a hexavalent uranyl species that arises from the formal loss of $H^{\bullet}$ from a methyl group on the acac ligand. This chemistry further confirms the need for a careful choice of supporting ligand for the synthesis of pentavalent uranyl complexes.

2.3. $[UO_2]^+$ complexes with oxo interactions with uranium or other metals

Upon one electron reduction, the two axial oxo atoms should exhibit a more pronounced Lewis basicity, in contrast to the unreactive $[UO_2]^{2+}$ oxo groups. As such, this should promote an increased ability of $[UO_2]^+$ to form compounds with cation–cation interactions.

Cation–cation interactions, or CCIs, form when a metal dioxo cation acts as a Lewis base ligand to another metal cation, see Fig. 3. In nuclear waste, dimers and aggregates form between different actinyl ions (particularly Np and Pu which have extra *f*-electrons), generating complex, and difficult to model mixtures [53].

These CCIs are very rare in hexavalent $[UO_2]^{2+}$ chemistry. They have been characterised in the solid state with alkali metals in a handful of crystal structures [54–56], with a second uranium in the tetrameric complex $[UO_2\{OCH(Pr^i)_2\}_2]_4$ **10** [57], which has remarkably basic oxo groups, and in the $[UO_2]^{2+}$-transition metal complexes $[UO_2(THF)(M\{THF\})L]$ **11** in which we used the constrained geometry of the macrocycle "L" to ensure the structures remain intact [58]. Notable also is the Lewis acid–base pair formed by coordination of tris(perfluorophenyl)borane to a uranyl complex to for the adduct **12** [59]. Thus, while the use of simple $[UO_2]^{2+}$ salts to model the more radioactive Np and Pu ions is too simplistic to correctly predict their behaviour, pentavalent uranyl complexes may provide significantly better functional models for their more radioactive neighbours.

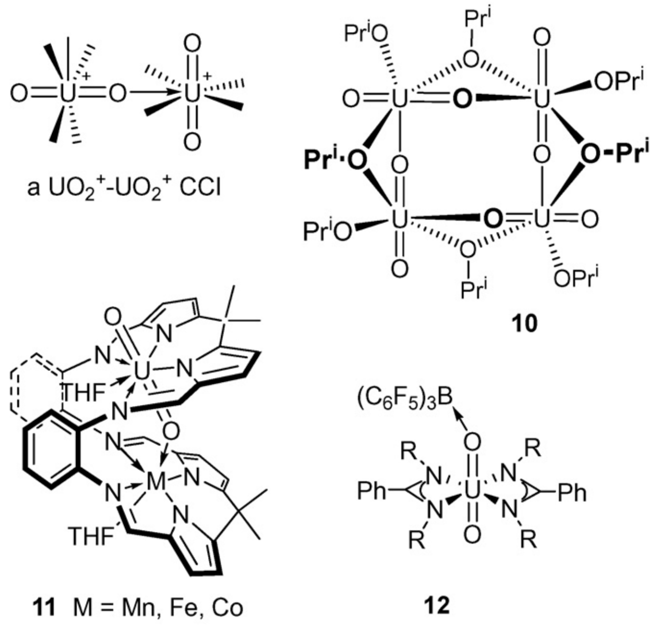


Fig. 3. A generic example of a cation–cation interaction (CCI), specific hexavalent $[UO_2]^{2+}$ compounds exhibiting CCIs and a borane adduct.

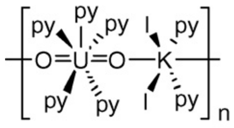


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Fig. 4. The repeating unit in the coordination polymer $\{[UO_2(py)_5][KI_2(py)_2]\}_n$ **13**.

Three years after the discovery of **4**, the isolation and characterisation of the pentavalent coordination polymer $\{[UO_2(py)_5][KI_2(py)_2]\}_\infty$ **13** was reported independently by Mazzanti and co-workers and Berthet and co-workers. Interestingly, the two routes to **13** derive from U^{III} and U^{VI} reagents, i.e. by the oxidation of $[UI_3(THF)_4]$ with pyridine-*N*-oxide and water[60] or by the reduction of $[UO_2I_2(THF)_3]$ with KC_5R_5 (R=H or Me) in pyridine, respectively [61]. Compound **13** has a pentagonal bipyramidal coordination geometry at the uranium centre with the axial positions occupied by the oxo ligands, and the equatorial sites occupied by the nitrogen atoms of the five pyridine ligands (Fig. 4).

Both oxo ligands are coordinated to a potassium ion resulting in the formation of a 1D chain with an average K–O distance of 2.84(7) Å. The uranium-oxo bond lengths range from 1.834(2) to 1.843(2) Å and are longer than those for hexavalent uranyl complexes. The polymeric nature of complex **13** can be explained by the increased ability of $[UO_2]^+$ to form cation–cation interactions compared to $UO_2{}^{2+}$ and reflect the more pronounced Lewis basicity of the axial oxygen atoms.

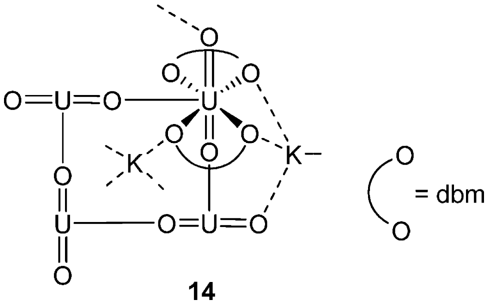
The uranyl asymmetric stretch for pentavalent uranyl complexes is observed in the IR spectrum at 797 cm^{-1} and is at significantly lower energy than the hexavalent $[UO_2I_2(py)_3]$ complex (927 cm^{-1}). The reproducible synthesis of complex **13** and the substitution reactions that it can undergo with organic ligands such as $OPPh_3$ and anionic salophen mean that it may be a versatile precursor for the synthesis of a variety of pentavalent uranyl complexes.

The ability of complex **13** to undergo substitution reactions has been exploited in the formation of $\{[UO_2(dbm)_2]_4[K_6(py)_{10}]\}.(I)_2.(py)_2$, **14**, a tetrameric cation–cation pentavalent uranyl complex that is made by reaction of **13** with dibenzoylmethanate (Eq. (2)).[52] The use of dbm as a ligand to support the formation of pentavalent uranyl complexes was reported previously in the electrochemical reduction of $[UO_2(dbm)_2(DMSO)]$; this compound was only characterised in solution and was not isolated [40].

$$\{[UO_2(py)_5][KI_2(py)_2]\}_n + 2\,\text{Kdbm} \xrightarrow{\text{pyridine}} \{[UO_2(dbm)_2]_4[K_6(py)_{10}]\}.(I)_2.(py)_2 \qquad (2)$$

The solid-state structure of **14** consists of four $[UO_2]^+$ ions arranged in a plane coordinated to two adjacent uranyl groups at two T-shaped cation–cation interactions (Fig. 5). The uranium metal centre is coordinated by two *trans* oxo ligands, four oxygen atoms from two bidentate dbm ligands and one bridging oxygen atom from an adjacent uranyl group resulting in a pentagonal bipyramidal geometry. Each oxo ligand is bound to either the uranium atom of the adjacent uranyl group or by a potassium ion resulting in a U—O═U═O—K motif.

Due to symmetry there are only two crystallographically distinct uranyl ions within the molecule. The interaction between the pentavalent uranyl groups results in significant elongation of the



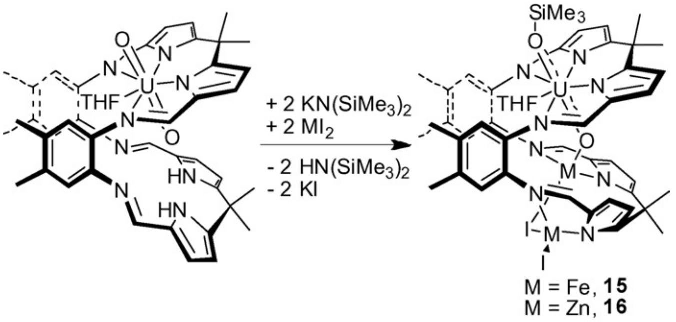
14

Fig. 5. Partial structural diagram for the tetramer $\{[UO_2(dbm)_2]_4[K_6(py)_{10}]\}.(I)_2.(py)_2$, **14**.

U=O groups in the U=O—U fragment to 1.923(10) and 1.934(8) Å. However, the other uranium-oxo bond lengths for the U=O—K fragment (1.828(10) and 1.811(9) Å) are comparable to those for **13** (1.834(2)–1.843(2) Å). This lengthening of the U=O bond is reflected in the IR spectrum of the complex, which exhibits an absorption at 782 cm^{-1} as compared to that of the starting material **13** (797 cm^{-1}). Characterisation of the pentavalent uranyl complex **14** by solution NMR spectroscopy in pyridine confirms that the solid-state structure observed is retained in solution, since the spectrum contains resonances consistent with a C_{4h} symmetric species. However, dissolution of **14** in DMSO provides a simpler NMR spectrum consistent with the disruption of the cation–cation interactions and the formation of a monomeric species. Complex **14** decomposes rapidly in pyridine solution to form unidentified U^{VI} and U^{IV} species, but it is more stable in DMSO, supporting the hypothesis that the disproportionation of pentavalent uranyl involves inner-sphere cation–cation ($[UO_2]^+{}_2$) interactions [53].

It is clear that the choice of ligand is important in order to isolate stable $[UO_2]^+$ complexes and to avoid known decomposition pathways. In conjunction with this Arnold, Love, and co-workers have found that the choice of ligands may even provide a way of supporting very unusual chemistry for the uranyl dication. The polypyrrolic macrocycle (H_4L) used to make **11**, Fig. 3, which upon metal-complexation folds to form a Pacman structure, provides a unique way of introducing reagents to the oxo-groups of the uranyl dication and has been shown to facilitate chemistry more reminiscent of transition metal dioxo congeners. The complex $[UO(OSiMe_3)(THF)Fe_2I_2L]$ [62], **15**, is a reductively functionalised pentavalent uranyl complex that was synthesised from its hexavalent precursor $[UO_2(THF)(H_2L)]$[63] by reaction with $KN(SiMe_3)_2$ and FeI_2 in THF (Scheme 3). Uniquely, **15** is a stable $[UO_2]^+$ cation–cation complex in which the *exo*-oxo group (with respect to the macrocyclic cleft) has reacted to form selectively a covalent bond with a trimethylsilyl group.

The mechanism for this reaction is as yet unknown, although it is hypothesised that the deprotonation of $[UO_2(THF)(H_2L)]$ with $KN(SiMe_3)_2$ results in the formation of $[UO_2(THF)(K_2L)]$ which is a highly reactive and oxidising species in which the two potassium ions coordinate to the *endo*-oxo ligand. It appears that the potassium cations influence the bonding of the uranyl dication such that a single electron transfer reaction occurs that results in the selective homolytic cleavage of the N–Si bond of the $HN(SiMe_3)_2$ by-product to form the singly covalently functionalised pentavalent complex **15**. Substitution of the potassium cations with transition metal cations aids the isolation of stable complexes that were characterised in the solid state. Significantly, the isolation of the d^{10} Zn(II) compound $[UO(OSiMe_3)(THF)Zn_2I_2L]$ **16**, confirms that the transition metal simply stabilises the pentavalent fragment, and does not participate in the redox chemistry observed.



Scheme 3. Synthesis of the reductively silylated $[UO(OSiMe_3)]^+$ complexes **15** and **16**.

In the solid-state structure of **15**, the uranium metal centre contains a *trans* dioxo at the axial positions and the equatorial sites are occupied by the four nitrogen atoms of the macrocycle and also the oxygen atom of a bound THF molecule resulting in a distorted pentagonal bipyramidal geometry. The *exo*-oxo ligand is bound to a silicon atom and the *endo*-oxo ligand forms a dative bond to an iron cation. The uranium-oxo bond lengths support the presence of U^V ($U{=}O_{endo}$ 1.870(4) Å, $U{=}O_{exo}$ 1.993(4) Å). These bond lengths are shorter than the U–O bond length found in the tetravalent U-$OSiR_3$ complex $Cp'_2U(OSiMe_3)CN$, where $Cp' = C_5H_2(CMe_3)_3$ (2.104 (4) Å)[64] and implies that the $U{=}O_{exo}$ bond retains some multiple bond character but less than that of the $U{=}O_{endo}$ bond. The variable temperature solid-state magnetic behaviour of the UZn_2 $f^1d^{10}d^{10}$ system of **16** shows a distinct decrease in moment with decreasing temperature upon descending from 300 K to 150 K, associated with the depopulation of excited crystal field states of the U^V f^1 cation, and below this continues to decrease with decreasing temperature, confirming the continued presence of a single unpaired electron. This rules out the presence of the more common f^2 U^{IV} oxidation state in which spin-pairing would reduce significantly the moment and remove any temperature dependence [21,65].

2.4. *Solid-state oxide compounds containing the U^V cation*

The only conclusive reports of naturally occurring oxide minerals containing U^V are the carbonate wyartite, $CaU^V(U^{VI}O_2)_2(CO_3)O_4(OH)(H_2O)_7$ [66], “dehydrated wyartite”, $Ca(CO_3)[U^V(U^{VI}O_2)_2O_4(OH)](H_2O)_3$ [67], and a radiation and thermally damaged zircon in which U^V replaces Zr^{IV} as an impurity [68]; none contain any pentavalent uranyl ion.

A small number of U^V oxide compounds have also been synthesised, by solid-state reactions under controlled oxygen fugacities, but again none contain a pentavalent uranyl moiety, e.g. AUO_3 (A = Na, K, Rb, $Ba_{0.5}$) [69,70], SrU_2O_6 [71], $USbO_5$ [72], and UVO_5 [73], the silicates $K(UO)Si_2O_6$ [74], and $K_3(U_3O_6)(Si_2O_7)$, and a germanate analogue, $Rb_3(U_3O_6)(Ge_2O_7)$ [75]. Also very recently $[U^V(H_2O)_2(U^{VI}O_2)_2O_4(OH)](H_2O)_4$ was made by reduction of $[UO_2]^{2+}$ ions with zinc and hydrazine at 120 °C for three days [76]. These were synthesised at high temperature, and/or pressure, and the latter four also under hydrothermal conditions. In each case, a combination of the polyhedral geometry, the bond-valence sum incident at the U site, electroneutrality requirements, X-ray photoelectron spectroscopy, and magnetic susceptibility data are used to support the presence of U^V.

3. Conclusions

Recent advances in air sensitive chemistry have made the isolation and characterisation of kinetically inert pentavalent uranyl complexes possible. The $[UO_2]^+$ cation has been isolated as molecular and polymeric compounds, and has been characterised in the solid state as well as in solution. It is evident that the ligand environment plays a vital role in the synthesis and the stability of $[UO_2]^+$ complexes, and careful consideration is required for the expansion of further synthetic routes. In general, the $[UO_2]^+$ ion exhibits reduced bonding to the oxo ligands and the equatorial ligands, as characterised by the elongated bond lengths observed in the solid state and the decrease in stretching frequency seen by IR spectroscopy. Reduction of hexavalent uranyl to pentavalent uranyl can result in increased Lewis basicity of the oxo ligands, which can lead to coordination of metal ions to the oxo groups and the formation of cation–cation interactions. The importance of these CCIs is already well-known for the more radioactive actinide dioxo cations formed by uranium's heavier neighbours neptunium and plutonium. It will be interesting to see how the spectroscopic and chemical reactivity studies will inform our understanding of real-world actinide chemistry, such as the formation of CCIs in nuclear wastes, and the reductive precipitation of uranyl salts from groundwater streams.

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