Versatile new uranyl(VI) dihalide complexes supported by tunable organic amide ligands†

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A series of uranyl(VI) dihalide complexes $UO_2X_2L_2$ (X = Cl, Br) supported by organic amide ligands (L = R′C(O)NR$_2$; R′ = *i*-Pr; R = *i*-Pr, *i*-Bu, *s*-Bu) offers the versatile combination of facile synthesis using benchtop methods, air-stable crystalline solids obtained in high yield, high solubility in common organic solvents and tunable steric/electronic properties.

Uranyl(VI) halides are an important facet of actinide chemistry due to the environmental relevance of these species in highly saline conditions (*i.e.*, brines associated with salt formations) and as precursors to new uranyl(VI) coordination complexes.[1] Of particular interest to synthetic chemists are *anhydrous* neutral uranyl(VI) dihalide systems that can serve as suitable starting materials in non-aqueous solvents. However, although new chloride,[2,3] bromide,[4] and iodide[5] derivatives continue to be reported, the synthetic utility of these compounds remains limited by a combination of low solubility and/or hydrolytic instability. For example, adducts such as $UO_2Cl_2(OPPh_3)_2$ are air-stable but rendered virtually insoluble in all common solvents.[6] Alternatively, $[UO_2Cl_2(THF)_2]_2$ is currently finding use as perhaps the most widely used precursor for new uranyl(VI) species,[3] yet this compound suffers from moisture sensitivity and limited solubility in donor solvents such as THF.[7]

Therefore, access to non-aqueous uranyl(VI) dihalide complexes of the general formula $UO_2Cl_2L_2$ possessing the following characteristics is highly desired: (1) high-yield benchtop synthesis from readily available starting materials; (2) stability with respect to hydrolysis; (3) good solubility in common organic solvents, including *hydrocarbon* solvents such as toluene; (4) tunability through modification of the steric and/or electronic properties of L. In this paper we report the synthesis and structural characterization of new uranyl(VI) complexes that meet all of the above criteria, including both chloride and bromide derivatives. As described below, the key to this versatility originates with the choice of aliphatic *N,N*-dialkyl amides (R′C(O)NR$_2$) as the neutral donor L.
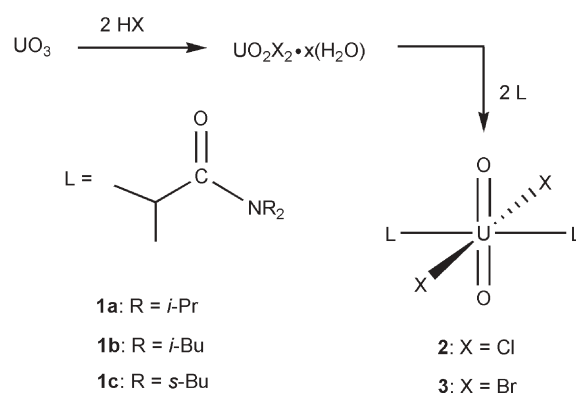
Organic amides have featured prominently in processing actinides from spent nuclear fuel,[8] such as the use of aliphatic malonamides for selective actinide extraction in the DIAMEX process,[9] and lactams used to precipitate uranyl(VI) species from

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† Electronic supplementary information (ESI) available: Synthetic procedures and spectroscopic data for **1–3**, Tables S1–S3, Fig. S1, and X-ray crystallographic files in CIF format for **2a** and **3c**. See DOI: 10.1039/b512966d

nitric acid solutions.[10] However, while this chemistry is dominated by nitrate complexation, considerably less attention has been given to the coordination chemistry of amides with uranyl(VI) halide complexes.[11] Previous studies were thwarted by the poor solubility offered by the relatively small amides used, and structural characterization was not reported. For our purposes the use of bulkier amides leads to more satisfactory results.

Following the synthetic procedure for $[UO_2Cl_2(THF)_2]_2$,[3] the dissolution of UO_3 in conc. HX (X = Cl, Br) generates the hydrated uranyl(VI) dihalide species $UO_2X_2 \cdot x(H_2O)$. The addition of 2 equivalents of the appropriate organic amide **1** to a methanol solution of this compound affords the corresponding air-stable uranyl(VI) adduct (**2**: X = Cl; **3**: X = Br) as a crystalline yellow solid in high yield (87–95%) after workup in CH_2Cl_2/heptane (Scheme 1). Compounds **2** and **3** exhibit excellent solubility in methanol, CH_2Cl_2, and THF, and are moderately soluble in benzene and toluene.

Single crystals suitable for X-ray crystallography were obtained for **2a** and **3c**.[12] A thermal ellipsoid drawing of **2a** is shown in Fig. 1. The bromide complex **3c** crystallizes with two independent molecules in the asymmetric unit; a thermal ellipsoid drawing for one of these representations is shown in Fig. S1.†

Both **2a** and **3c** display similar structural features in the solid state with an octahedral coordination geometry for the uranium center, and as this central atom sits on an inversion center a bond angle of 180° subtends all mutually *trans* ligands, consisting of *trans* oxo ligands, *trans* chloride donors, and the carbonyl oxygen atoms belonging to the *trans* amide ligands. The bond distances for the uranyl(VI) unit (between 1.741(5) Å and 1.770(2) Å), as well as the U–X bonds (U(1)–Cl(1) = 2.6468(8) Å, U(1A)–Br(1A) = 2.8153(7) Å, U(1A)–Br(1A) = 2.8127(7) Å), are all within the
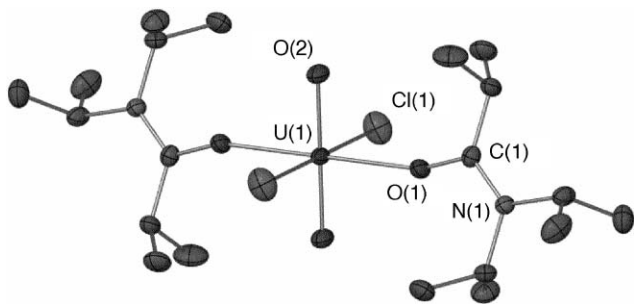

Scheme 1

Fig. 1 Thermal ellipsoid drawing of **2a**, showing thermal ellipsoids at 50% probability. Selected bond distances (Å) and bond angles (°): U(1)–O(1), 2.3151(18); U(1)–O(2), 1.770(2); U(1)–Cl(1), 2.6468(8); O(1)–C(1), 1.270(3); O(2)–U(1)–O(2), 180.00(12); U(1)–O(1)–C(1), 160.83(18).

normal range of reported uranyl(VI) chloride[13] and bromide[4,14] complexes.

In contrast, the U–O$_{(amide)}$ bond distances range between 2.281(4)–2.3151(18) Å, which are decidedly shorter than those found in uranyl(VI) amide complexes (typically 2.34–2.40 Å),[15] suggesting stronger bonding to the uranium center. Indeed, these U–O bond distances are similar to those found in complexes involving hard phosphine oxide ligands (O=PR$_3$),[16] which are known to coordinate very strongly to the uranyl(VI) ion. The increased electron donation from the amide ligands coincides with a notable weakening of the carbonyl unit, as indicated by a significantly reduced $\nu_{C=O}$ stretch from that of the free amide (typically by 70 cm^{-1}), a feature that applies for all of the uranyl(VI) amide complexes reported here. The relatively open U–O–C bond angles (160.83(18)–171.9(5)°) are evidently linked to these short U–O bonds, following a trend that has been noted in a compilation of uranyl amide complexes showing an inverse correlation between these two parameters.[10] For example, the longest bond distance (U(1)–O(1) = 2.3151(18) Å) and the smallest bond angle (U(1)–O(1)–C(1) = 160.83(18)°) are both found in **2a**, perhaps reflecting a lesser need for electron donation from the amide ligands in the presence of the chlorides, in comparison to stronger amide–metal bonding in **3c** to compensate for the weaker bromide donors.

There is no discernible preference for the orientation of the π-system associated with the amide plane (defined by the atoms connected to the sp^2-hybridized atoms C(1) and N(1)) with respect to the remainder of the uranium coordination sphere. This is most notable in the discrepancy between the tilt angles observed in the two independent molecules in **3c**, where in one complex the amide unit is aligned almost coplanar with the Br–U–Br axis, while in the other this plane is offset by approximately 30°.

Finally, it is worth noting that the choice of alkyl substitution on the amide ligands is essential to providing the suitable electronic and steric balance necessary for **2** and **3** to serve as viable anhydrous uranyl(VI) reagents. As noted previously, the use of small acetamides yields uranyl chloride adducts with very low solubility. On the other hand, our attempts to prepare uranyl(VI) halide complexes with amide ligands possessing *increased* steric bulk (*i.e.*, *t*-Bu) in the R′ group lead to compounds that are highly hydroscopic. We suspect that since the amides adopt a

conformation that directs the bulkier *N*,*N*-dialkyl substituents away from the uranium center, this places the *t*-Bu group attached to the carbonyl carbon in a sterically unfavorable position that hinders effective binding of the amide oxygen atom. Thus, we have found an effective combination of air stability and favorable solubility with R′ = *i*-Pr, with further tuning possible through variation of the alkyl substituents R on the amide N atom. Our initial efforts with these systems indicate that the solubility and steric protection provided by these amides offer a distinct advantage that has enabled us to isolate the first structurally characterized example of a uranyl(VI) complex possessing unsupported thiolate ligands.[17] We are investigating further the synthetic utility of these new uranyl(VI) starting complexes.

Notes and references

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12 Crystallographic data for **2a**: C$_{20}$H$_{42}$Cl$_2$N$_2$O$_4$U, F_w = 683.49, monoclinic, $P2_1/c$, a = 8.5267(4), b = 11.3761(5), c = 13.8153(6) Å, β = 96.7450(10)°, T = 173(2) K, V = 1330.82(10) Å^3, Z = 2, λ = 0.71073 Å, ρ_{calc} = 1.706 g cm^{-3}, μ = 6.324 mm^{-1}, 9261 reflections measured, 2905 unique, R_{int} = 0.0185, wR_2 = 0.0494 (all data), GOF = 1.128; Crystallographic data for **3c**: C$_{20}$H$_{50}$Br$_2$N$_2$O$_4$U, F_w = 828.51, monoclinic, $P2_1/c$, a = 16.8340(11), b = 14.0098(9), c = 14.4084(9) Å, β = 106.0300(10)°, T = 173(2) K, V = 3266.0(4) Å^3, Z = 4, λ = 0.71073 Å, ρ_{calc} = 1.605 g cm^{-3}, μ = 7.444 mm^{-1}, 22823 reflections measured, 7182 unique, R_{int} = 0.0314, wR_2 = 0.0744 (all data), GOF = 1.154. CCDC 283797 and 283798. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512966d.
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