



Uranyl complexes with 1,2-diols and tetrahydrofurfuryl alcohols

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ABSTRACT

2,3-Dimethyl-2,3-butanediol (pinacol, L^1) reacted with uranyl nitrate and acetate hydrates to give $[\text{UO}_2(\text{NO}_3)_2(L^1)] \cdot L^1$ (**1**· L^1) and $[\text{UO}_2(\text{OAc})_2(L^1)]$ (**2**), while 2,5-dimethyl-3,4-di-iso-propyl-3,4-hexanediol (L^2) was found to undergo a pinacol rearrangement into the ketone $R_3\text{CCOR}$ ($R = i\text{Pr}$) in the presence of uranyl complexes. Treatment of $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ with tetrahydrofurfuryl alcohol (L^3) and α,α -ditertibutyltetrahydrofurfuryl alcohol (L^4) led to the formation of $[\text{UO}_2(\text{NO}_3)_2(L^3)] \cdot \text{H}_2\text{O}$ (**3**· H_2O) and $[\text{UO}_2(\text{NO}_3)_2(L^4)]$ (**4**). The crystal structures show that the metal coordination is similar in the 1,2-diol and ether–alcohol complexes but, in contrast to **1**· L^1 , **2** and **3**· H_2O which form one- or two-dimensional hydrogen bonded assemblages, the structure of **4** is composed of discrete molecules, due to the lack of intermolecular hydrogen bonds. The crystal structure of uncomplexed L^2 is also described.

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1. Introduction

Actinide complexes with diol ligands are very rare, being limited to a few uranyl derivatives. In the hydroxylamide and 1,4-naphthalene dicarboxylate (NDC) compounds $[\text{UO}_2(\text{NH}_2\text{O})_2(\text{HOCH}_2\text{CH}_2\text{OH})]$ [**1**] and $[\text{UO}_2(\mu\text{-NDC})(\text{HOCH}_2\text{CH}_2\text{OH})]$ [**2**], the coordinated 1,2-diol comes from the use of ethylene glycol as solvent during the synthesis. We reported the crystal structure of $[\text{UO}_2(\text{NO}_3)_2(\text{HOCMe}_2\text{CMe}_2\text{OH})]$ (**1**), isolated from a 1:1 mixture of $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ and pinacol (L^1 , Scheme 1) in THF [**3**]. Similar reaction of uranyl nitrate hexahydrate with $\text{HOCr}_2\text{CH}_2\text{CH}_2\text{CR}_2\text{OH}$ ($R = \text{Me}, t\text{Bu}$) gave second sphere complexes in which the 1,4-diols are hydrogen bonded to the water and nitrate oxygen atoms of the $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ moiety. Following these studies, we tried to enlarge this series of complexes by changing both the uranyl salt UO_2X_2 and the substituents of the α -diol $\text{HOCR}_2\text{CR}_2\text{OH}$. Here we present a new crystalline form of **1** as the solvate **1**· L^1 , and the crystal structure of the acetate analogue $[\text{UO}_2(\text{OAc})_2(L^1)]$ (**2**). Our attempts at the coordination of $\text{HOCiPr}_2\text{CiPr}_2\text{OH}$ (L^2) were impeded by the pinacol rearrangement of the diol into the ketone $R_3\text{CCOR}$ ($R = i\text{Pr}$) which was catalysed by UO_2X_2 ($X = \text{NO}_3, \text{Cl}; \text{X}_2 = \text{SO}_4$), but the crystal structure of L^2 was determined. We were also interested in the complexation of the uranyl unit by alkoxy-alcohol molecules, in particular tetrahydrofurfuryl alcohol (L^3) and α,α -ditertibutyltetrahydrofurfuryl alcohol (L^4), this latter having been obtained from the reaction of $t\text{Bu}_2\text{CO}$ with sodium in THF. While compounds of main group and d transition metals with tetrahydrofurfuryl alcohols were considered as polymerisation catalysts

[**4**] or precursors in sol–gel and metal–organic chemical vapour processes [**5**], no such complexes of the f elements were reported. Here we present the synthesis and X-ray crystal structure of $[\text{UO}_2(\text{NO}_3)_2(L^3)] \cdot \text{H}_2\text{O}$ (**3**· H_2O) and $[\text{UO}_2(\text{NO}_3)_2(L^4)]$ (**4**).

2. Results and discussion

2.1. Uncomplexed diol L^2 and alkoxy alcohol L^4

The α -diol L^2 was synthesized in 36% yield by reaction of diisopropyl ketone with 1 mol equivalent of lithium in THF, following a modification of the procedure described by Nasarov who used sodium in diethyl ether [**6**]. Crystals of L^2 suitable for X-ray diffraction were grown by slow evaporation of a pyridine solution. A view of one of the three independent and quite identical molecules in the asymmetric unit is shown in Fig. 1a and selected hydrogen bonding distances and angles are listed in Table 1. These molecules are close to the gauche conformation, with O1–C1–C2–O2 torsion angles of 47.3(3)°, 47.2(3)° and 47.6(3)° for molecules A, B and C, respectively. Such a conformation minimizes the steric interactions between the staggered $i\text{Pr}$ groups (the terminal carbon atoms are further directed away from one another) and it is further stabilized in this case by an intramolecular O2–H···O1 hydrogen bond involving the two hydroxyl groups. The second hydroxyl proton in each molecule is involved in an intermolecular O1–H···O2 hydrogen bond, with formation of two sets of zigzag chains, one containing the A and B and the other the C molecules (Fig. 1b). By comparison with the less congested pinacols $\text{HOCR}_2\text{CR}_2\text{OH}$, the O1–C1–C2–O2 torsion angles in L^2 are smaller than those of 64(1)° ($R = \text{H}$) [**7a**] or 62.5(4)° ($R = \text{Me}$) [**8a**], while the central C1–C2 distance of 1.612(2) Å is significantly larger than those

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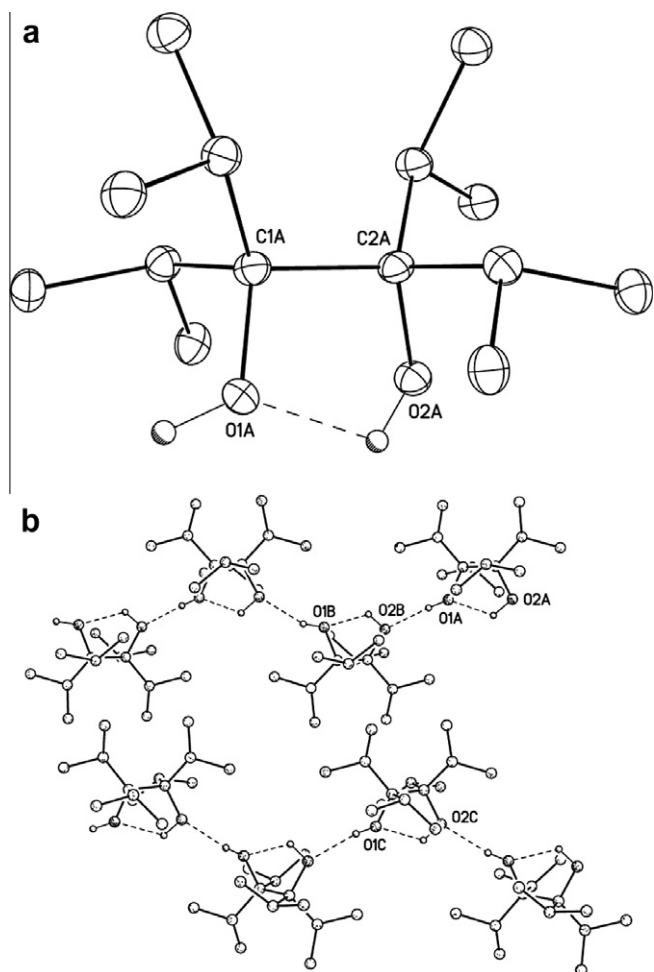


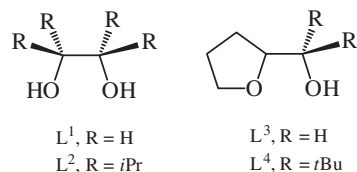
Fig. 1. (a) View of one of the three independent and quite identical molecules in the asymmetric unit of L^2 . Displacement ellipsoids are drawn at the 30% probability level. (b) View of the hydrogen bonded assemblage. The hydrogen atoms not involved in hydrogen bonding are omitted for clarity. Hydrogen bonds are represented as dashed lines.

Table 1
Hydrogen bonding interactions: selected distances (Å) and angles ($^\circ$).

	D...A	D–H	H...A	D–H...A
L^2	O1A...O2B	2.904(3)	0.92	2.00
	O1B...O2A'	2.902(3)	0.94	2.04
	O1C...O2C''	2.907(3)	0.89	2.07
	O2A...O1A	2.552(4)	0.96	1.94
	O2B...O1B	2.537(3)	0.90	1.96
	O2C...O1C	2.552(3)	0.91	1.96
$1 \cdot L^1$	O3...O7	2.709(5)	0.94	1.78
	O7...O4'	3.191(5)	0.95	2.28
2	O3...O8'	2.666(7)	1.00	1.82
	O4...O5''	2.725(6)	0.99	1.79
$3 \cdot H_2O$	O4...O11	2.620(13)	0.91	1.71
	O11...O7'	3.127(13)	0.88	2.32
	O11...O10''	3.043(11)	0.96	2.11
4	O4...O9	2.554(5)	0.88	2.26

Symmetry codes: L^2 : ' = $x, y + 1, z$; '' = $1/2 - x, y + 1/2, 1/2 - z$. $1 \cdot L^1$: ' = $-x, -y, -z$. **2**: ' = $1/2 - x, -y, z$; '' = $1 - x, y, 3/2 - z$. $3 \cdot H_2O$: ' = $-x, y - 1/2, 1/2 - z$; '' = $x + 1, y, z$.

measured in ethylene glycol (1.5089(6) Å by X-ray diffraction [7a] and 1.475(6) Å by neutron diffraction [7b]) and in pinacol (1.544(4) [8a] and 1.527(4) Å [8b]).



Scheme 1. The diols L^1 , L^2 and the tetrahydrofurfuryl alcohols L^3 and L^4 .

Similar treatment of ditertibutyl ketone with sodium in diethyl ether did not afford the corresponding 1,2-diol but gave a mixture of the alcohol tBu_2CHOH and the 1,4-diol $HOtBu_2CH_2CH_2CtBu_2OH$ [9]. These two products were also obtained when the reaction was performed in THF, but in this solvent the formation of α, α -ditertibutyltetrahydrofurfuryl alcohol (L^4) was observed in addition; L^4 was isolated as an oil after chromatography, with a 26% yield. The synthesis of L^4 which likely resulted from the coupling of the ketyl and THF radicals, is reminiscent of the formation of the α, α -dicyclopopyltetrahydrofurfuryl alcohol in the reaction of dicyclopopylketone and potassium in THF [10]. Such THF adducts were also obtained as by-products during the Sml_2 -mediated coupling reactions between iodoalkynes and ketones or aldehydes [11] in THF, and L^4 was indeed previously synthesized in 54% yield from the reaction of phenyl iodide and ditertibutyl ketone in the presence of Sml_2 [11c].

2.2. Uranyl complexes with 1,2 diols

Yellow crystals of $[UO_2(NO_3)_2(L^1)] \cdot L^1$ ($L^1 = HOtMe_2CMe_2OH$) (**1**· L^1) were obtained in almost quantitative yield by cooling a hot chloroform solution of a 1:2 mixture of uranyl nitrate hexahydrate and pinacol. The crystal structure (Fig. 2a) exhibits a plane of symmetry passing through the U, O1, O2 atoms and the middle of the central C–C bond of the bidentate L^1 ligand which is disordered over two positions. The geometrical parameters of the hexagonal bipyramidal uranium environment (Table 2) are quite identical to those measured in the structure of **1** [3], with average U–O(uranyl), U–O(nitrate) and U–O(pinacol) distances of 1.749(5), 2.498(12) and 2.436(3) Å, respectively. The C1A and C1B atoms of the central C–C bond of the pinacol are on either side of the mean equatorial plane, with out-of-plane distances of 0.544 and -0.415 Å, respectively. The pinacolic C–C distance of 1.636(13) Å of the coordinated diol in **1**· L^1 is abnormally large by comparison with those of 1.568(9) Å in the L^1 solvate molecule, 1.544(4) Å in free pinacol [8a] and 1.457(12) Å in **1** [3]; this apparent discrepancy is certainly due to the disorder of the carbon skeleton in L^1 resulting in a slightly erroneous bond length determination. Four uranyl complexes **1** are connected to each L^1 solvate molecule via hydrogen bonds (two as donors and two as acceptors) so as to create a two-dimensional assembly with a distorted square grid pattern parallel to the ab plane (Fig. 2b and Table 1). Both the complex unit and the free L^1 molecule display hydroxyl protons directed laterally and are thus donors in two divergent hydrogen bonds; since they are approximately at right angle to one another, the hydrogen bonding pattern extends in a plane.

Treatment of $[UO_2(OAc)_2(H_2O)_2]$ with 1 mol equivalent of L^1 in chloroform gave yellow crystals of $[UO_2(OAc)_2(L^1)]$ (**2**). A view of **2** is shown in Fig. 3a and selected bond distances and angles are listed in Table 2. The structure of **2** is similar to that of **1**, the κ^2 nitrate being replaced with κ^2 acetate ligands. The mean U–O(uranyl) and U–O(pinacol) bond distances of 1.773(2) and 2.472(4) Å are similar to those measured in **1** and **1**· L^1 . The C1 and C2 atoms of the pinacolic bond are displaced from the mean equatorial plane, by 0.643 and -0.387 Å, respectively. The C1–C2 distance of 1.498(13) Å is quite identical to that measured in **1**. The average

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