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The Reduction of Uranium Tetrachloride by Lithium Tetrahydroaluminate in Tetrahydrofuran or Dimethoxyethane

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The use of $LiAlH_4$ saturated solutions in tetrahydrofuran and dimethoxyethane media as reducing agent is reported. The obtained products are easily isolable from the reaction mixture and correspond to the composition $LiU_2Cl_7 \cdot 9/2S$ and $UCl_3 \cdot 3/2S'$ respectively (S = tetrahydrofuran and S' = dimethoxyethane).

Introduction

So far the coordination and organometallic chemistry of uranium(III) have been scarcely investigated, mainly due to the easy oxidation [1] of U^{3+} derivatives in aqueous and non-aqueous media causing difficult handling, as well as to the very low solubility of simple salt-like halides which are the most common starting materials. Only quite recently some halide complexes with convenient solubility properties in non-aqueous solvents have been described [2, 3].

We report here on the results obtained in reducing UCl_4 in tetrahydrofuran (THF) and dimethoxyethane (DME) by $LiAlH_4$, in an alternative procedure to Moody's method [2]. The advantage of using $LiAlH_4$ as a reducing agent consists mainly in the more rapid reduction of UCl_4, due to its appreciable solubility in the solvents employed.

Experimental

Materials

UCl_4 was prepared according to reported method [5], $LiAlH_4$, 18-crown-6, 2,2'-bipyridine were commercially available reagent grade products. The solvents were purified by refluxing over potassium in the presence of benzophenone as an oxygen indicator, followed by distillation under a nitrogen atmosphere. This method did not work with dimethoxyethane containing appreciable amounts of peroxides, here the solvent was first refluxed over $NaBH_4$ and KOH.

Visible-NIR and IR spectra were recorded on a Cary 17 D Varian and on a Perkin-Elmer Mod. 580 B spectrophotometers, respectively.

IR spectra of the obtained products were scanned as nujol mulls and are reported in Fig. 2.

C, H, N, elemental analysis was carried out by Mr. A. Berton of this Institute; Cl was determined potentiometrically, U gravimetrically and Li by flame emission spectroscopy.

Coordinated THF and DME molecules were determined by gas chromatographic analysis after decomposition of the sample with HCl in toluene.

All manipulations were carried out in an oxygen- and moisture-controlled dry box, since the products are extremely air sensitive.

Reduction in tetrahydrofurane

To 500 mg of UCl_4 (1.3 mmol) in 30 ml of THF, 1 ml of a saturated solution of $LiAlH_4$ in the same solvent was added dropwise under stirring. Gas evolution occurred, the solution became red, and a red brown precipitate separated. After two hours of stirring, the solution was filtered off and the solid washed with several portions (5 ml) of THF and then dried under vacuum (yield = 70–80%).

Anal. Calcd. for $LiU_2Cl_7 \cdot 9/2THF$: Li, 0.66; U, 45.05; Cl, 23,58; C, 20.46; H, 3.41; THF, 30.71%. Found: Li, 0.53; U, 43.49; Cl, 23.33; C, 17.89; H, 2.94; THF, 30.41%.

The product is rather insoluble in THF, in spite of the bright red color of the solution.

Reduction in dimethoxyethane

UCl_4 (500 mg, 1.3 mmol) was suspended in 30 ml of DME and 1 ml of a saturated solution of $LiAlH_4$ in the same solvent was added. Immediate formation of a brown precipitate occurred with gas evolution, while the supernatant liquid became colorless after 0.5 hour stirring. The solid was collected by filtration, washed with several portions (5 ml) of DME and vacuum dried.

Anal. Calcd. for $UCl_3 \cdot 3/2DME$: U, 49.64; Cl, 22.18; C, 15.03; H, 3.13; DME, 28.16%. Found: U, 47.79; Cl, 22.17; C, 14.79; H, 3.17; DME, 27.17%.

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The product is quite insoluble in DME, but soluble in THF giving a red purple solution (the 300–1700 nm spectrum is reported in Fig. 1 curve C).

On further addition of $LiAlH_4$-saturated solution to the UCl_3 suspension, the supernatant liquid got progressively red and with a large excess of the reducing agent (about over ten times the stoichiometric ratio) a metallic mirror separated on the walls of the reaction vessel.

The 300–1700 nm spectrum of the red solution is reported in Fig. 1 curve A.

By stirring a mixture of insoluble $UCl_3 \cdot 3/2DME$ with LiCl in DME the liquid became red coloured, the 300–1700 nm spectrum is reported in Fig. 1 curve B.

Reaction with 18-crown-6

Approximately 1.5 mmol of $UCl_3 \cdot 3/2DME$ and $LiU_2Cl_7 \cdot 9/2THF$ were brought into reaction in DME and THF respectively with 2 mmol of 18-crown-6.

The mixtures were stirred overnight. Pink insoluble solids were separated, washed with the appropriate solvent and vacuum dried.

Anal. Calcd. for $(UCl_3)_3$(18-crown-6$)_2$: U, 45.72; Cl, 20.43; C, 18.46; H, 3.07%. Found (from $UCl_3 \cdot 3/2$-DME): Cl, 20.22; C, 19.11; H, 3.12%. Found (from $LiU_2Cl_7 \cdot 9/2THF$): Cl, 20.13; C, 18.16; H, 3.21%.

The same reaction was carried out using UCl_3-$(THF)_x$ prepared as reported in ref. 2. Analytical data and the infrared spectrum (s. Fig. 2) turn out to be identical to the above ones.

Reaction with 2,2′-bipy

The reaction was carried out as described for 18-crown-6. In this case a bright green product slightly soluble was isolated following the usual work-up. *Anal.* Calcd. for $UCl_3 \cdot 3/2bipy$: U, 41.13; Cl, 18.38; C, 31.13; H, 2.07; N, 7.26%. Found (from $UCl_3 \cdot$-3/2DME): Cl, 18.14; C, 30.21; H, 2.14; N, 6.93%. Found (from $LiU_2Cl_7 \cdot 9/2THF$): Cl, 17.95; C, 29.19; H, 2.17; N, 6.87%.

Results and Discussion

Solutions of $LiAlH_4$ in THF and DME prove to be useful reducing agents towards UCl_4 dissolved in the same solvents. The nature of the products depends, however, both on the type of the solvent and on the molar ratio of the $LiAlH_4$ as far as DME is concerned. In any case the obtained products have a well defined composition and are easily separable from the reaction media.

In THF solution a complex of a composition corresponding to $LiU_2Cl_7(THF)_{9/2}$ is obtained and the reduction may be described by the following scheme:

$$4UCl_4 + LiAlH_4 \longrightarrow 4UCl_3 + LiCl + AlCl_3 + 2H_2 \quad (1)$$

$$4UCl_3 + 2LiCl + 9THF \longrightarrow 2LiU_2Cl_7(THF)_{9/2} \quad (2)$$

The LiCl necessary to complex UCl_3 is supplied by the collateral reaction of exceeding $LiAlH_4$ with $AlCl_3$ [4] formed in (1):

$$3LiAlH_4 + AlCl_3 \longrightarrow 4AlH_3 + 3LiCl \quad (3)$$

$LiU_2Cl_7(THF)_{9/2}$ is a dark purple, very sensitive material which is rather insoluble in THF, in spite of the bright red colour of solutions. Its infrared spectrum (Fig. 2) presents the absorption bands found in other THF complexes, but at present it is not possible to decide if THF is coordinated to U, to Li, or to both. By increasing the molar ratio of $LiAlH_4$ the composition of the reduced product remains unchanged. On the contrary, in DME solution a greenish material with composition corresponding to UCl_3-$(DME)_{3/2}$ is obtained if the value of the $LiAlH_4/UCl_4$ molar ratio is one; it is nearly insoluble in DME and also extremely air sensitive. By further addition of the reducing agent a complicated reaction and formation of a mixed brown and mirror like material occurs under gas evolution, while the solution becomes

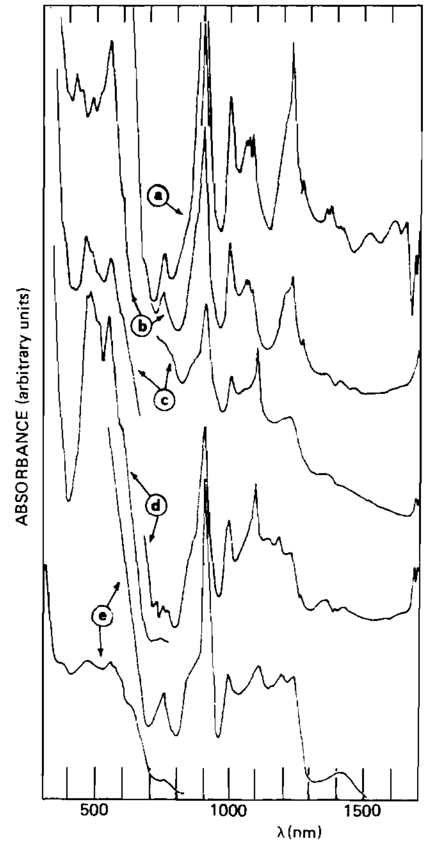

Fig. 1. Absorption spectra of: A. $UCl_4 + LiAlH_4$ excess in DME; B. $UCl_3(DME)_{3/2}$ + LiCl in DME; C. $UCl_3(DME)_{3/2}$ in THF; D. $UCl_4 + LiAlH_4$ in THF($LiU_2Cl_7 \cdot (THF)_{9/2}$; E. $UCl_3(THF)_x$ in THF ref. 2.

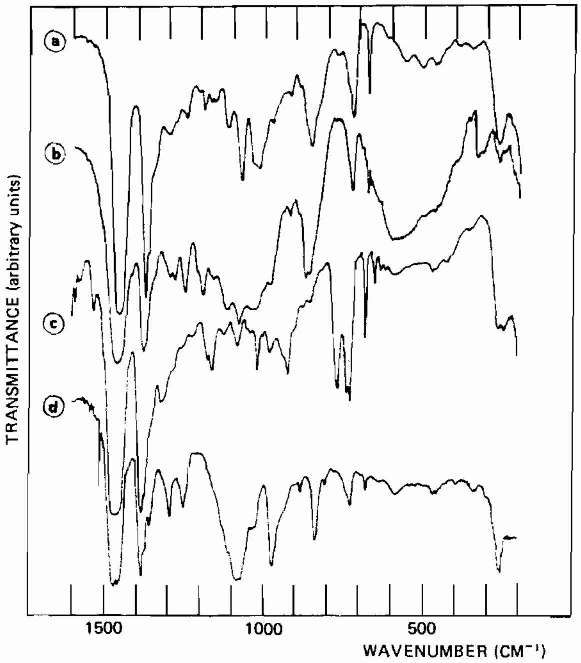

Fig. 2. Infrared spectra (Nujol mulls) of the species: A. $LiU_2Cl_7(THF)_{9/2}$; B. $UCl_3(DME)_{3/2}$; C. $UCl_3(bipy)_{3/2}$; D. $(UCl_3)_3(18\text{-crown-}6)_2$.

progressively red purple. Thus it can be argued that at the beginning a simple reduction such as:

$$4UCl_4 + LiAlH_4 + DME \longrightarrow 4UCl_3(DME)_{3/2} + LiCl + AlCl_3 + 2H_2 \quad (4)$$

takes place, a soluble complex by reaction of $UCl_3(DME)_{3/2}$ with LiCl is formed. At this point, a great excess of $LiAlH_4$ may push the reduction to metallic uranium (as indicated by the appearance of the mirror material). We did not investigate the nature of the red coloured solution, but these assumptions seem confirmed by the comparison of the 300–1700 nm spectra of the solution containing UCl_4 + excess $LiAlH_4$ (curve A Fig. 1) and of a solution obtained by stirring insoluble $UCl_3(DME)_{3/2}$ with excess of LiCl (curve B, Fig. 1) which are almost identical. In the latter case it is reasonable to suppose the formation of the anionic chloride species, which are probably also present in the former solution.

The optical spectra reported in Fig. 1 are quite similar, particularly concerning the position of the bands, the main difference between the spectra registered in DME and those registered in THF being in the changed relative intensity of the bands located in the range 1000–1250 nm. Moreover, these spectra are analogous to that reported in ref. 2 for the complex $UCl_3(THF)_x$.

This indicates that the environment of the uranium central atom is practically the same; the spectra of $UCl_3(THF)_x$ and that of $UCl_3(DME)_{3/2}$ in THF suggest the occurrence of the displacement of DME by THF:

$$UCl_3(DME)_{3/2} + xTHF \longrightarrow UCl_3(THF)_x + 3/2DME$$

This behaviour may be explained on the basis of a stronger solvating power of THF with respect to DME and a larger lattice energy of $UCl_3(DME)_{3/2}$.

Reaction of $LiU_2Cl_7(THF)_{9/2}$, and $UCl_3(DME)_{3/2}$ with strong Lewis bases such as 2,2'-bipy and 18-crown-6 gives rise to substitution of LiCl, THF and DME and formation of the new very air sensitive complexes: $UCl_3(bipy)_{3/2}$ (yellow-green) and $(UCl_3)_3(18\text{-crown-}6)_2$ (pink)*.

The infrared spectra (1300–600 cm^{-1}) reported in Fig. 2 show absorption bands analogous to those of other metal complexes containing the same ligands [8–13], thus indicating that DME and bipy are chelated, while the exact mode of ligation of 18-crown-6 at present cannot be established. However the coordination number of the central atom in $UCl_3(DME)_{3/2}$ and $UCl_3(bipy)_{3/2}$ for instance would be higher than six (which is the apparent one) because oligomerization phenomena due to chloride bridges may be involved, even though in lesser extent than in pure UCl_3 [14].

In conclusion, the reduction of UCl_4 with $LiAlH_4$ in THF or DME media is a rapid and simple way to prepare uranium(III) halide complexes which may be employed as starting materials for further reactions in the field of coordination and organometallic chemistry.≠

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*It has been reported that other uranium(III) derivatives such as $UCl_3(THF)_x$ [6] and $NH_4UCl_4 \cdot 5H_2O$ [7] by reaction with 18-crown-6 form the complex $UCl_3 \cdot 18\text{-crown-}6$.

≠At present the reactions of $LiU_2Cl_7(THF)_{9/2}$ and $UCl_3(DME)_{3/2}$ with lithium or magnesium alkyls and K_2COT (COT = dianion of cyclooctatetraene), respectively, are under investigation. In particular with K_2COT a dismutation is observed with the formation of $UCOT_2$ and a very reactive form of metallic uranium which in turn reacts with cyclooctatetraene to give $UCOT_2$ again.

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