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Preparation and characterization of an (iodobutoxy)-[hydridotris(3,5-dimethylpyrazol-1-yl)borate]uranium complex

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Abstract

During the reaction of a uranium pellet with freshly sublimed elemental iodine in THF, ring opening of the THF was observed and a U^{IV} species was obtained. Further reaction of the solution with $Na[HB(3{,}5Me_2pz)_3]$ in THF at room temperature gave, after recrystallization, a green crystalline solid **2** formulated as $[UI_2\{O(CH_2)_4I\}\{HB(3{,}5\text{-}Me_2pz)_3\}]$ on the basis of various analyses. This complex has also been prepared by reaction of UI_4 in THF with the potassium salt of the polypyrazolylborate. The mechanism of the ring-opening of THF is discussed.

1. Introduction

We have been using poly(pyrazolyl)borates as stabilizing ligands for the syntheses of Ln^{III}, U^{III}, U^{IV} and Th^{IV} complexes [1–3]. For An^{IV}, a variety of stable alkoxide derivatives has been synthesized by reaction of $[AnCl_2\{HBpz_3\}_2]$ and $AnCl_3\{HB(3{,}5\text{-}Me_2pz)_3\}\text{-}THF]$ ($An = U^{IV}$ or Th^{IV}) with alcohols or the corresponding respective alkoxides [4–8].

In an attempt to synthesize a iodouranium(III) complex with $[HB(3{,}5\text{-}Me_2pz)_3]$ we treated uranium metal with iodine in THF and added to this solution a sodium salt of the pyrazolylborate. The product was a uranium(IV) species which contained iodobutoxide arising from the opening of the THF ring during the oxidation of the uranium metal by elemental iodine. Here we report the isolation of the solid complex **2**, its characterization, and the mechanism of formation of the iodobutoxide ligand.

2. Experimental section

2.1. Materials and methods

All operations were performed in an argon-filled glove-box or using Schlenk and vacuum-line techniques.

Tetrahydrofuran, toluene and hexane were dried by refluxing, under argon, with Na/K alloy and were distilled immediately before use. The solvents were degassed on the vacuum line before use. Benzene-d_6 was dried over Na. The sodium salt $NaHB(3{,}5\text{-}Me_2pz)_3$ was prepared as described for the potassium salt [9]. The uranium pellet was kindly provided by Dr. J.C. Spirlet of the Institute for Transuranium Elements, Joint Research Centre, Karlsruhe.

Proton NMR spectra were recorded using Bruker SY80FT and AM 200 NMR spectrometers. The chemical shifts are reported in ppm relative to Me_4Si. Infrared spectra were recorded using Perkin Elmer 577 and 883 spectrophotometers; the samples were prepared as Nujol mulls between CsI plates but the iodobutanol was examined neat between CaF_2 plates. Elemental analyses were performed using a Perkin Elmer 2400 automatic analyser. Mass spectra (MS)

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data were determined on an Ribermag R-100 gas chromatograph/mass spectrometer. GC analyses were performed on a Carlo Erba Fractovap 2150 capillary gas chromatograph using a 25 m BP1 capillary column connected to a computing integrator.

2.2. Synthesis of 2

2.2.1. Method A

A uranium pellet was washed several times with concentrated HNO_3, H_2O, and acetone and dried under vacuum in a Schlenk vessel. This Schlenk vessel was transferred to an argon-filled glove-box, the uranium metal suspended in THF and 40 mg of HgI_2 added. When the solution turned blue, the uranium pellet was separated, washed with THF and dried under vacuum. The shiny metal (3.9 g) was transferred to an argon-filled glove-box, suspended in about 70 ml of THF, and 1.1 g of freshly sublimed elemental iodine was added slowly without any cooling during the reaction. The reaction mixture was stirred for about 24 h. The excess of metal (3.4 g) was separated from the solution by filtration and the content of uranium was determined gravimetrically on an aliquot. We designate the species in solution as **1**.

For analyzing species **1** the solvent was evaporated giving a brown oil. It was dissolved in THF and gave a solution which yielded the following data. UV-vis-NIR absorption spectrum in THF solution (v_{max}): 780w, 820w, 910w, 1050s, 1160w, 1260s, 1450w nm. ^1H NMR (C_6D_6): −11.5 (THF), −16.4, (THF), 198.5 (2H, $CH_2(O(CH_2)_4I)$), 80.6 (2H, $CH_2(O(CH_2)_4I)$), 48.5 (2H, $CH_2(O(CH_2)_4I)$), 23.6 (2H, $CH_2(O(CH_2)_4I)$).

Based on the content of uranium and on the volume of the solution of **1**, 650 mg (2.03 mmol) of $NaHB(3,5\text{-}Me_2pz)_3$ in THF was added slowly (ratio of borate/uranium = 1/1). After reaction overnight, the suspension was centrifuged and the supernatant liquid evaporated to dryness. The resulting solid was recrystallized from a mixture of toluene and hexane. The green solid **2** was separated from the supernatant liquid and dried under vacuum (yield 41%). IR: 2540m (B–H), 1525s, 1400s, 1370s, 1340s, 1185s, 1060s, 1035s, 975w, 835w, 800s, 685w, 640w, 460vw 350vw cm^{-1} UV-vis-NIR absorption spectrum in THF solution (ν_{max}) 640m, 660m, 770vw, 815vw, 885vw, 960w, 1030s, 1100s, 1200w, 1280w, 1380w, 1430w nm. Anal. Calcd for $C_{19}H_{30}BI_3N_6OU$: C 23.1; H 2.95; N 8.5 U 24.1. Found: C 24.2; H 3.0; N 8.3; U 22.8% ^1H NMR (C_6D_6): −23.39 (6H, *Me*(pz)), −19.09 (2H, *H*(4)(pz)), −10.72 (6H, *Me*(pz)), 26.55 (3H, *Me*(pz)), 55.93 (3H, *Me*(pz)), 60.83 (1H, *H*(4)(pz)), 21.00 (2H, $CH_2(O(CH_2)_4I)$), 45.49 (2H, $CH_2(O(CH_2)_4I)$), 78.73 (2H, $CH_2(O(CH_2)_4I)$), 189.39 (2H, $CH_2(O(CH_2)_4I)$).

2.2.2. Method B

A uranium pellet was washed several times with concentrated HNO_3, H_2O and acetone and dried under vacuum in a Schlenk vessel. This uranium pellet (1.54 g, 6.47 mmol) reacted overnight in vacuum at 500°C with an excess of freshly sublimed iodine (5.08 g, 20 mmol of I_2) as described earlier [10]. The black powder obtained was heated overnight at 160°C under vacuum to volatilize iodine and yielded the UI_4. (Anal. Calcd for I_4U: I 68.1; U 31.9. Found: I 66.2 U 31.0%.) A suspension of UI_4 (217 mg, 0.29 mmol) in THF (10 ml) was stirred for about one how, when it changed from bright red to bright green. (UV-vis-NIR absorption spectrum in THF solution (ν_{max}) 500vs, 600vs, 640vs, 780w, 820w, 910w, 1050s, 1160w, 1260s, 1450w nm.). Then $KHB(3,5\text{-}Me_2pz)$ (97.5 mg, 0.29 mmol) in THF was added. After overnight reaction, the suspension was centrifuged, the bright green solution separated from the precipitate, and the solvent removed under vacuum. The green solid obtained was recrystallized from toluene/hexane and vacuum dried (yield 42%). Anal. Found: C 21.7; H 2.90 N 8.3%. All the other data agree with those obtained using method A.

2.3. Hydrolysis of 1 or 2 to give 4-iodobutanol

A sample of complex **2** was treated with 0.1 N HCl, followed by ether extraction. The organic phase was separated and washed with 0.1 N $Na_2S_2O_3$ and with water, dried over $MgSO_4$, and filtered. The filtrate was concentrated in vacuum and the yellow product obtained was analyzed. IR (neat sample): 3320s (OH), 2920s, 2860s, 1420s, 1440sh, 1210s, 1160s cm^{-1}. ^1H NMR ($CDCl_3$): 3.75 (1H, O*H*), 3.65 (2H, t, CH_2), 3.20 (2H, t, CH_2), 1.9 (2H, m, CH_2), 1.65 (2H, m, CH_2). MS *m/e*: 200 (0.59, M^+), 73 (82.61, M − I), 55 (100, M − I − H_2O). These values were identical with the ones given by an authentic sample of 4-iodobutanol prepared as previously described [11], by reaction of $ISiMe_3$ with THF.

A solution of the species **1** (30 ml containing 1.95 mol of U) was hydrolyzed and, after treatment as above, the resulting product was identified as 4-iodobutanol (yield 45%). UI_4 (620 mg, 0.83 mmol) was stirred in 20 ml of THF and hydrolyzed. After treatment 4-iodobutanol was isolated (yield 60%).

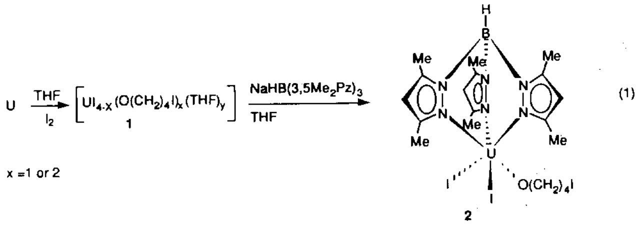
3. Results and discussion

By reaction of freshly sublimed iodine with a pellet of uranium in THF without controlling the temperature, we obtained mainly a U^{IV} species **1**, as shown by its electronic absorption spectrum in THF instead of $UI_3(THF)_4$ described by Sattelberger and collaborators [12]. In the near IR region a manifold of weak absorption bands was observed, the most intense being centred at 1050 and 1260 nm, which is not consistent with a U^{III} species.

A solution of **1** reacts with $NaHB(3,5\text{-}Me_2pz)_3$ in 1:1 stoichiometric ratio to give, after recrystallization from toluene/hexane, a green complex formulated as $[UI_2\{O(CH_2)_4I\}\{HB(3,5\text{-}Me_2pz)_3\}]$ (**2**) on the basis of elemental analysis, ^1H NMR, absorption electronic and infrared spectroscopies. We confirmed iodobutoxide by hydrolysis. The organic compound thus obtained was identified as 4-iodobutanol by comparison with an authentic sample. The complex **2** is quite soluble in THF and in aromatic solvents and slightly soluble in aliphatic solvents.

Other U^{IV} complexes containing $HB(3,5\text{-}Me_2pz)_3$ are known and X-ray structural analysis and ^1H NMR spectra have been reported. These complexes are seven or six coordinate, depending on the particular ligands present, the coordination around the metal being octahedral or capped octahedral [3,13]. In solution they are static and the pattern obtained for the protons of the pyrazolyl rings is consistent with the symmetry of the complexes in the solid state. For the complex $[UI_2\{O(CH_2)_4I\}\{HB(3,5\text{-}Me_2pz)_3\}]$ (**2**) no X-ray structural study was undertaken but the ^1H NMR spectrum at 300 K shows a pattern for the methyl groups and for the protons of the pyrazolyl rings consistent with an octahedral geometry around the metal. Two of the pyrazolyl rings are magnetically equivalent and the third is different. The resonances due to the magnetically equivalent rings, which are *trans* to the halogens, appear at high field and the resonances due to the third ring appear at low field, which is a pattern commonly observed for complexes of the type $[UCl_2X\{HB(3,5\text{-}Me_2pz)_3\}]$ ($X = OR, NR_2, C_5H_5$ or R) previously synthesized [3,5,7,8]. For the iodobutoxide we observed four resonances of equal intensity which have very large chemical shifts and line widths (*ca.* 20 Hz). This broadening obscures any multiplicity. These results are comparable with earlier results obtained for analogous U^{IV} complexes of the type $[UCl_2(O^iPr)\{HB(3,5\text{-}Me_2pz)_3\}]$ [7] and $[UCl_2\{OCH(C_2H_5)_2\}\{HB(3,5\text{-}Me_2pz)_3\}$ [8]. Chemical shifts and line widths of the resonances in f-element compounds depend in a complex way on the nature of the paramagnetic centre, the ligands, and the geometry [14]. ^1H NMR for $[UCl_2\{OCH(C_2H_5)_2\}\{HB(3,5\text{-}Me_2pz)_3\}$ in C_6D_6: −28.30 (6H, *Me* (pz)), −15.90 (2H, *H* (4) (pz)), −10.60 (6H, *Me* (pz)), 20.90 (3H, *Me* (pz)), 53.41, (1H, *H* (4) (pz)), 56.88 (3H, *Me* (pz)), 31.41 (6H, *Me* (OR)), 65.48 (2H, C*H*$_2$ (OR)), 69.31 (2H, C*H*$_2$ (OR)), 144.90 (1H, C*H* (OR)).

The iodobutoxide coordinated to the uranium(IV) is formed during the oxidation of uranium metal by I_2. However all attempts to characterize fully the uranium(IV) species **1** formed in this reaction failed. We always obtained after evaporation of the THF an oil unsuitable for elemental analysis. This oil was very soluble in benzene and toluene but recrystallization from toluene/hexane or benzene/hexane never succeeded. Hydrolysis of the oil always gave 4-iodobutanol. The presence of THF coordinated to the uranium(IV) was also confirmed by the ^1H NMR spectrum: two signals of equal intensity at −11.5 and −16.4 in benzene-d_6, were not apparent in THF-d_8. Four signals of equal intensity with chemical shifts at 198.5, 80.6, 48.5, 23.6, in benzene-d_6 are also consistent with coordinated iodobutoxide. The species **1** is probably $UI_{4-x}\{O(CH_2)_4I\}_x(THF)_y$ ($x = 1$ or 2), and an iodide or an iodobutoxide can be then substituted by the hydrotris(3,5-dimethylpyrazol-1-yl)borate to yield complex **2** (eqn. (1)).



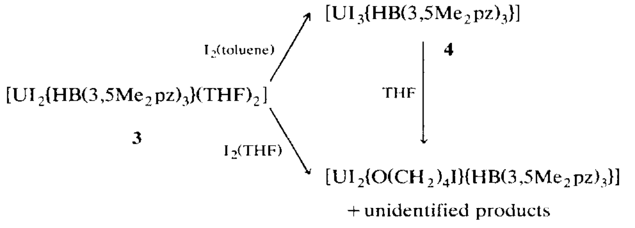
The preparation of tetravalent iodides and their reactivities have been reported by du Preez *et al.* but all the reactions were performed in acetonitrile or in methylene chloride [15]. We synthesized UI_4 according to the method of Bagnall *et al.* [10]. The absorption electronic spectrum of its solution in THF is characteristic of U^{IV} species and in the range 780–1450 nm coincides with the absorption electronic spectrum obtained for species **1**. We verified that hydrolysis of this solution gives 4-iodobutanol with a yield of 60%. By adding to this solution a stoichiometric amount of $KHB(3,5\text{-}Me_2pz)_3$, we were able to isolate the complex **2** in a yield of 42% (eqn. (2)).

$$UI_4 \xrightarrow{THF} \Big[\underset{\mathbf{1}}{UI_{4\text{-}x}(O(CH_2)_4I)_x(THF)_y}\Big] \xrightarrow[THF]{KHB(3,5Me_2Pz)_3} \underset{\mathbf{2}}{[UI_2\{O(CH_2)_4I\}\ \{HB(3,5Me_2Pz)_3\}]} \qquad (2)$$

$x = 1$ or 2

The complex $[UI_2\{HB(3,5\text{-}Me_2pz_2)_3\}(THF)_2]$ (**3**) was prepared by reaction of $[UI_3(THF)_4]$ with $Na[HB(3,5\text{-}Me_2pz)_3]$ in THF [16]. The analogous U^{IV} complex $[UI_3\{HB(3,5\text{-}Me_2pz)_3\}]$ (**4**) was obtained by reaction of complex **3** with an equimolar amount of I_2 in toluene or benzene [17]. Its ^1H NMR spectrum in benzene-d_6 shows three signals at 6.99 (1H, *H*(4)pz), 4.72 (3H, *Me*(pz)) and −7.57 ppm (3H, *Me* (pz)), a pattern identical to the one obtained for known complex

$[UCl_3\{HB(3,5\text{-}Me_2pz_2)_3\}]$ [3].

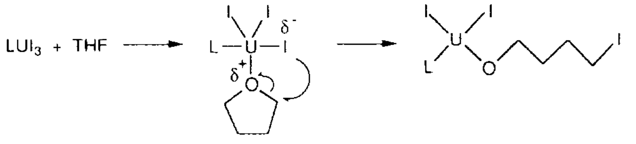


However, if reaction of **3** with iodine is conducted in THF we obtained a mixture of species where the complex **2** was easily identified by its ^1H NMR spectrum instead of the complex **4**. We also observed complex **2** when complex **4** was left in THF. The ^1H NMR spectra showed the total disappearance of complexes **3** and **4**. These reactions were studied by ^1H NMR spectroscopy, and unidentified products make the exact yields of the reactions difficult to evaluate. These results suggest that ring-opening of THF occurs with uranium(IV) iodides such as **4** and UI_4.

The formation of the species **1** can be explained by the opening of THF by UI_4. This derivative would have been formed during the attempted preparation of $[UI_3(THF)_4]$ according to the procedure of Sattelberger [12], as we did not maintain the temperature at 0°C and an excess of uranium was used.

Ring opening reactions of THF involving lanthanide and actinide derivatives have been known for many years [18–31]. Formation of iodoesters by opening of THF by acid chlorides mediated by SmI_2 has been observed, and similarly reactions of acid chlorides with yttrium chlorides yield chloroesters [18–20]. Phosphide or pentamethylcyclopentadienyl lead to various lanthanide complexes or organic molecules, with opening of THF [21–23]. In the last reactions, an oxonium ion is formed by the Lewis acid lanthanide and the $C_5Me_5^-$ or PPh_2^- is the attacking nucleophile. This mechanism was first proposed for THF polymerizations [24]. The higher the Lewis acidity of the metal, the easier the reactions. Ferric chloride induces opening of THF but ferrous chloride forms a stable complex with THF [25]. Rates for cleavage of ethers follow the Lewis acid strength: $AlCl_3 < AlBr_3 < AlI_3$ [26].

The formation of the iodobutoxide is explained by a similar mechanism: the uranium is a Lewis acid and the nucleophile is coordinated iodide. Uranium(IV) butoxide has been isolated in the reaction of UCl_3 with sodium cyclopentadienide [27]. Polymerization of THF was also observed with solutions of UCl_5 [28]. In the preparation of THF adducts of thorium tetrachloride or tetrabromide by the reaction of metal and elemental halogen in THF the yield decreased when the temperature was not maintained below 30°C and an oily product, which has not been characterized, was obtained. However, in that case, it was suggested that this compound is formed by opening of the THF ring during oxidation of the thorium [29].



L = I, HB(3,5-Me2Pz)3

The difference of reactivity between uranium(III) and (IV) iodide derivatives may be due to their different Lewis acidities. Only the stronger Lewis acids promote ring-opening of THF.

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References

1 A. Carvalho, A. Domingos, P. Gaspar, N. Marques, A. Pires de Matos and I. Santos, *Polyhedron, 11* (1992) 1481.
2 A. Domingos, J. Marçalo, I. Santos and A. Pires de Matos, *Polyhedron, 9* (1990) 1645.
3 A. Domingos, N. Marques and A. Pires de Matos, *Polyhedron, 9* (1990) 69.
4 A. Domingos, I. Santos and A. Pires de Matos, *J. Less Common Metals, 149* (1989) 279.
5 A. Domingos, J. Marçalo, N. Marques, A. Pires de Matos, K.W. Bagnall and J. Takats, *J. Less Common Metals, 149* (1989) 271.
6 A. Domingos, J. Marçalo, and A. Pires de Matos, *Polyhedron, 11* (1992) 909.
7 N. Marques, J. Marçalo, A. Pires de Matos, I. Santos and K.W. Bagnall, *Inorg. Chim. Acta, 134* (1987) 309.
8 T. Almeida, Diploma Thesis, Universidade de Lisboa (1987).
9 S. Trofimenko, *J. Am. Chem. Soc., 89* (1967) 5288.
10 K.W. Bagnall, D. Brown, P.J. Jones and J.G.H. du Preez, *J. Chem. Soc.*, (1965) 350.
11 W.P. Weber, *Silicon Reagents for Organic Synthesis*, 1983, Springer-Verlag.
12 D.L. Clark, A.P. Sattelberger, S.G. Bott and R.N. Vrtis, *Inorg. Chem., 28* (1989) 1771.
13 R.G. Ball, F. Edelman, J.G. Matisons, J. Takats, N. Marques, J. Marçalo, A. Pires de Matos and K.W. Bagnall, *Inorg. Chim. Acta, 132* (1987) 137.
14 R.D. Fisher, in T.J. Marks and I.L. Fragala (eds.), *Fundamental and Technological Aspects of Organo-f-Element Chemistry* Reidel, Dordrecht, 1985, 277.
15 (a) J.G.H. du Preez and B. Zeelie, *J. Chem. Soc., Chem. Commun.*, (1986) 743; (b) J.G.H. du Preez, B. Zeelie, U. Corsellato and R. Graziani, *Inorg. Chim. Acta, 129* (1987) 289.
16 J. Takats, unpublished results.
17 A. Pires de Matos and I. Santos, unpublished results.
18 J. Souppe, J.L. Namy and H.B. Kagan, *Tetrahedron Lett., 25* (1984) 2869.
19 S.M. Ruder, *Tetrahedron Lett., 33* (1992) 2621.
20 C. Qian, A. Qiu, Y. Huang and W. Chen, *J. Organomet. Chem., 412* (1991) 53.

21 H. Schumann, E. Palamidis and J. Loebel *J. Organomet. Chem., 384* (1990) C49.

22 W.J. Evans, T.A. Ulibarri, L.R. Chamberlain, J.W. Ziller and D. Alvarez Jr., *Organometallics, 9* (1990) 2124.

23 H. Yasuda, H. Yamamoto, K. Yokota and A. Nakamura, *Chem. Lett.,* (1989) 1309.

24 M.E. Woodhouse, F.D. Lewis and T.J. Marks, *J. Am. Chem. Soc., 104* (1982) 5586 and references therein.

25 J.R. Kern, *J. Inorg. Nucl. Chem., 24* (1962) 1105.

26 M.V. Bhatt and J.R. Babu, *Tetrahedron Lett., 32* (1984) 3497.

27 G.L. Ter Haar and M. Dubeck, *Inorg. Chem., 3* (1964) 1648.

28 A. Pires de Matos, unpublished results.

29 D.L. Clark, T.M. Frankcom, M.M. Miller and J.G. Watkin, *Inorg. Chem., 31* (1992) 1628.

30 Y. Tsuji, M. Kobayashi, F. Okuda and Y. Watanabe, *J. Chem. Soc., Chem. Commun.,* (1989) 1253.

31 A.B. McLaren, B. Kanellakopulos and E. Dornnberger, *Inorg. Nucl. Chem. Lett., 16* (1980) 223.