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Uranium(III) Poly(pyrazol-1-yl)borate Complexes*

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Abstract

Reactions of the adduct $UCl_3 \cdot (THF)_x$ (THF = tetrahydrofuran) with compounds of the type $K[H_nBL_{4-n}]$, where L = pyrazole or 3,5-dimethylpyrazole, are presented. Based on the results obtained the two compounds $UCl_2H_2BPz_2 \cdot THF$ and $UCl_2HBPz_3 \cdot THF$ were isolated.

Introduction

In previous work in our laboratories, studies of some uranium(IV) poly(pyrazol-1-yl)borate complexes by ^{11}B NMR spectroscopy were reported [1]. Reactions of uranium tetrachloride in tetrahydrofuran with the poly(pyrazol-1-yl)borates of potassium were tested. In this work we report analogous reactions with the uranium(III) adduct, $UCl_3 \cdot (THF)_x$ (THF = tetrahydrofuran).

The observations of the ^{11}B NMR spectra allowed the isolation of the compounds $UCl_2H_2BPz_2 \cdot THF$ and $UCl_2HBPz_3 \cdot THF$.

Electronic absorption spectra were also recorded in order to check if the U(III) species suffered oxidation or if the uranium(III) chloride adduct prepared, the starting metal halide, was free from uranium(IV) species.

Experimental

Physical and Analytical Measurements

^{11}B and ^1H NMR spectra were made using a NMR Multinuclear spectrometer Bruker SY80FT. Chemical shifts are referenced to $Si(CH_3)_4$ in the ^1H NMR and to KBH_4/D_2O in the ^{11}B NMR spectra. The solutions for NMR were prepared in a glove box and the NMR tubes sealed under vacuum. Deuterated tetrahydrofuran (THF-d_8) was dried over Na/benzophenone and degassed by freeze-thaw cycles on a vacuum line. Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer. Samples were prepared in a glove box as nujol mulls between CsI plates. Electronic absorption spectra in the visible and near IR region were recorded on a Cary 17 spectrophotometer with samples in solution. Elemental analyses were performed on a C,H,N automatic analyser. Samples were encapsulated in aluminium containers in a dry box.

Materials and Methods

All procedures were performed in Schlenk-type glassware interfaced to a vacuum (10^{-3}–10^{-4} torr) line, or in a nitrogen-filled glove box in which water and oxygen contents were lower than 10 ppm.

Tetrahydrofuran was dried over type 4 Å molecular sieves, distilled after refluxing with Na/K/benzophenone, and triply distilled from lithium aluminium hydride. Toluene and hexane were distilled from Na/K/benzophenone. UCl_4 was prepared by a published method [2]. $UCl_3 \cdot (THF)_x$ was prepared by reduction of UCl_4 with Na_2C_2 in tetrahydrofuran [3]. Na_2C_2 was obtained by heating in vacuum the monosodium acetylide, which was prepared as described [4]. The ligands $K[H_nBL_{4-n}]$ (L = pyrazole or 3,5-dimethylpyrazole) were prepared as published [5].

$UCl_2H_2BPz_2 \cdot THF$

Stoichiometric amounts of $UCl_3 \cdot (THF)_x$ and KH_2BPz_2 were stirred at room temperature in dry THF overnight. After centrifugation, the supernatant solution was vacuum-evaporated to dryness and the solid washed with dry and degassed hexane. The supernatant was removed and the solid was vacuum-dried overnight to give a lilac powder. *Anal.* Calc. for $UC_{10}H_{16}N_4Cl_2OB$: U, 46.0; C, 23.2; H, 3.1, N, 10.8. Found: U, 46.7, C, 23.2, H, 3.2; N, 10.9. ^1H NMR (in THF-d_8) (δ *vs.* Me_4Si) at 25 °C: 16.2(s), 10.9(s); 9.5 (s). ^1H NMR (in CD_3CN) (δ *vs.* Me_4Si) at 25 °C: 13.7 (s); 11.5(s), 9.1(s). Electronic spectrum (tetrahydrofuran solution). 745(sh), 870(sh); 910(vs); 1008(w); 1089(w), 1198(sh); 1229(sh); 1255(m) nm. Infrared spectrum (Nujol mull): B–H doublet centered at 2440 cm^{-1} and ν(U–Cl) 270 cm^{-1}.

$UCl_2HBPz_3 \cdot THF$

Stoichiometric amounts of $UCl_3 \cdot (THF)_x$ and $KHBPz_3$ were stirred at room temperature in dry

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THF. After centrifugation, the supernatant solution was vacuum-evaporated to dryness and the solid obtained washed with dry and degassed hexane. The supernatant was removed and the solid was vacuum-dried overnight to give a blue–green powder. *Anal.* Calc. for $UC_{13}H_{18}N_6Cl_2OB$: U, 40.8; C, 26.3; H, 3.0, N, 14.4. Found: U, 41.0; C, 24.8, H, 2.9, N, 13.7. ^1H NMR (in THF-d_8) (δ *vs.* Me_4Si) at 25 °C: 36.4(s); 22.1(s); 15.8(s). ^1H NMR (in CD_3CN) (δ *vs.* Me_4Si) at 25 °C: 27.7(s); 21.6(s); 16.0(s). Electronic Spectrum (Tetrahydrofuran solution). 770(sh); 915(vs); 1009(w); 1021(sh); 1088(w); 1207(sh), 1239(m); 1265(sh) nm. Infrared spectrum (nujol mulls): B–H mode at 2485 and ν(U–Cl) 270 cm^{-1}.

Results and Discussion

The ^{11}B NMR spectral parameters obtained in tetrahydrofuran for the reactions of the potassium salts of the various poly(pyrazol-1-yl)borates with the $UCl_3\cdot(THF)_x$, as well as the corresponding potassium salts, are shown in Table I.

The ^{11}B NMR spectra after addition of 1 equivalent of KH_2BPz_2, $KHBPz_3$ and $KH_2B(3,5\ Me_2Pz)_2$ to $UCl_3\cdot(THF)_x$ display only one single band at 25.0 ppm, 64.0 ppm and 57.7 ppm, respectively. Spectra of the solutions after addition of increasing quantities of the salts KH_2BPz_2 and $KH_2B(3,5\ Me_2Pz)_2$ show in each case another band near the position of the corresponding free ligands. The addition of more $KHBPz_3$ leads to insoluble species which could not be extracted by benzene or acetonitrile. The reactions with $KBPz_4$ leads to a spectrum with two bands at 63.0 ppm and 42.1 ppm. The addition of $KHB(3,5\ Me_2Pz)_3$ to the uranium(III) adduct gave a spectrum with bands at 50.5 ppm and 34.2 ppm, for any stoichiometry used. However the species corresponding to the 50.5 ppm seems to be unstable as this line disappears if the reactions are left overnight.

The observation of one single line displaced from the position of the free ligand when we added $KHBPz_3$ or KH_2BPz_2 to $UCl_3\cdot(THF)_x$ in the stoichiometric quantities 1:1 indicated coordination of the ligands to the paramagnetic centre. Based on these observations we were able to prepare the solid complexes $UCl_2H_2BPz_2\cdot THF$ and $UCl_2HBPz_3\cdot THF$ which were characterized by elemental analysis, electronic absorption spectroscopy, ^1H NMR and vibrational spectroscopy.

As was recently discussed by Marks *et al.* [6], barriers to progress in trivalent uranium chemistry have included the intractability of uranium trichloride prepared by conventional routes [7, 8] and the lack of suitable ligands.

We believe that the poly(pyrazol-1-yl)borates are suitable ligands for U(III) as they are described as stabilizing unusual coordination geometries and

TABLE I. ^{11}B Chemical Shifts of the Titration of $UCl_3\cdot(THF)_x$ with $K[H_nBL_{4-n}]$ (L = pyrazole or 3,5-dimethylpyrazole, n = 0, 1, 2) in THF Solution

Samples	δ (ppm)	w^b (ppm)
KH_2PBz_2	33.2 (t)^a	2.5^a
$UCl_3\cdot(THF)_x + KH_2BPz_2$	25.0	4
$UCl_3\cdot(THF)_x + 2KH_2BPz_2$	25.0; 33.2	4, 3
$UCl_3\cdot(THF)_x + 3KH_2BPz_2$	25.0, 33.2	4; 3
$KHBPz_3$	39.2 (d)^a	3.0^a
$UCl_3\cdot(THF)_x + KHBPz_3$	64.0	7
$UCl_3\cdot(THF)_x + 2KHBPz_3$	–	–
$UCl_3\cdot(THF)_x + 3KHBPz_3$	–	–
$KH_2B(3,5\ Me_2Pz)_2$	29.5 (t)^a	3.0^a
$UCl_3\cdot(THF)_x + KH_2B(3,5\ Me_2Pz)_2$	57.7	7
$UCl_3\cdot(THF)_x + 2KH_2B(3,5\ Me_2Pz)_2$	57.7, 29.5	7, 4
$UCl_3\cdot(THF)_x + 3KH_2B(3,5\ Me_2Pz)_2$	57.7; 29.5	7, 4
$KBPz_4$	42.6 (s)^a	0.25^a
$UCl_3\cdot(THF)_x + KBPz_4$	63.0, 42.1	–
$UCl_3\cdot(THF)_x + 2KBPz_4$	63.0, 42.1	–
$UCl_3\cdot(THF)_x + 3KBPz_4$	63.0; 42.1	–
$KHB(3,5\ Me_2Pz)_3$	35.4 (d)^a	3.5^a
$UCl_3\cdot(THF)_x + KHB(3,5\ Me_2Pz)_3$	50.5, 34.2	6, 4
$UCl_3\cdot(THF)_x + 2KHB(3,5\ Me_2Pz)_3$	50.5; 34.2	6, 4
$UCl_3\cdot(THF)_x + 3KHB(3,5\ Me_2Pz)_3$	50.5, 34.2	6; 4

[a] Values from reference [1], [b] Line width in ^1H-decoupled spectrum External reference and lock KBH_4/D_2O.

oxidation states, due to their steric and electronic properties [9].

Considering some conventional routes to prepare the uranium trichloride adduct [7, 8], apart from being time consuming they also need an exact control over the reaction time as well as concentration of the reagents. Although the recently reported method for the preparation of $UCl_3 \cdot (THF)_x$ [3], reduction of the uranium(IV) halide with Na_2C_2 (which we used throughout this work), shows some advantages over the previous ones, the preparation does not always give the same yield, even with the same experimental conditions. In some cases, the reduction of the U(IV) to U(III) species is not complete, which could be easily detected by further reaction of the uranium halide adduct with the potassium poly(pyrazol-1-yl)-borates and observation of the ^{11}B NMR spectrum of the solution. In one of the reactions with $KHBPz_3$ we detected the contamination with U(IV) species. Besides the band at 64 ppm (U(III)) we could see another, weaker band at 10 ppm, assigned to a uranium(IV) species as reported previously in our laboratories [1]. This contamination was also confirmed by electronic absorption spectra where we could see some of the U(IV) characteristic bands (1174 nm(s), 1118 nm(s), 1109 nm(s), 1075 nm(s)).

All reactions were followed by ^{11}B NMR and electronic absorption spectroscopy before we proceeded to isolate any solid compound.

Work is in progress in our laboratories in an attempt to prepare the uranium(III) compounds with the other ligands.

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