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^{11}B NMR Studies on some Uranium(IV) Poly(pyrazol-1-yl) Borate Complexes

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Results from ^{11}B NMR spectroscopy of compounds of the type $UCl_x[H_nBL_{4-n}]_{4-x}$ where L = pyrazole or 3,5-dimethylpyrazole are presented. In contrast with all the compounds studied which display only a single peak, $UCl_2[HB(3,5\text{-}Me_2Pz)_3]_2$ and $UCl_2[H_2B(3,5Me_2Pz)_2]_2THF$ have more complicated spectra. This is explained in terms of disproportionation reactions of these more labile compounds due to the bulky methylated ligands.

Introduction

Although no full X-ray structural data are available yet for the actinide complexes of the poly(pyrazol-1-yl) borates, a good deal of information has been obtained from their electronic and ^1H NMR spectra [1–3]. In this work we present some data on ^{11}B NMR spectra for the uranium compounds of this type. In spite of the broad lines observed, the spectra are simple, and in some cases the large chemical shifts of some paramagnetic species can be useful in their characterization.

Experimental

The preparation and handling of all the compounds were carried out in an inert atmosphere glove box (O_2, $H_2O < 20$ ppm). All solvents were purified and dried by standard methods.

Infrared spectra were recorded using a Perkin Elmer 577 spectrophotometer with samples mounted as nujol mulls between CsI plates.

Electronic absorption spectra were recorded using a Cary 17 Varian spectrophotometer with samples in solution.

The ^{11}B NMR spectra were made in a NMR multinuclear spectrometer Bruker SY 80 FT.

The compounds $UCl_2[HBPz_3]_2$, $U[HBPz_3]_4$, $UCl_2[BPz_4]_2$, $UCl_2[HB(3,5\text{-}Me_2Pz)_3]_2$, $U[H_2B(3,5\text{-}Me_2Pz)_2]_4$, $UCl_2[H_2B(3,5\text{-}Me_2Pz)_2]_2 \cdot THF$ were prepared by published methods [1–3].

The compound $UCl_3HB(3,5\text{-}Me_2Pz)_3THF$ was prepared by stirring together in tetrahydrofuran at room temperature stoichiometric amounts of UCl_4 and $KBH(3,5\text{-}Me_2Pz)_3$, vacuum drying the supernatant solution after centrifugation, washing with pentane, and vacuum drying again. The analysis of a green-turquoise powder obtained gave: U, 34.0%; Cl, 14.8%; C, 31.6%; H, 4.0%; N, 11.9% (calculated for $UCl_3HB(3,5\text{-}Me_2Pz)_3THF$: U, 33.4%; Cl, 14.9%; C, 32.0%; H, 4.2%; N, 11.8%).

Results and Discussion

The ^{11}B NMR spectra parameters for the uranium poly(pyrazol-1-yl) borates and the corresponding potassium salts are shown in Table I. With the exception of $KBPz_4$ the other potassium salts display very broad lines (about 75 Hz). The uranium compounds display still broader lines, as expected, and in some cases the coupled spectra gave unresolved bands.

In contrast with all the compounds shown in Table I, $UCl_2[HB(3,5\text{-}Me_2Pz)_3]_2$ (I) and $UCl_2[H_2B(3,5\text{-}Me_2Pz)_2]_2THF$ (II), display two peaks instead of one. In order to obtain more information about these compounds we followed the titration of UCl_4 in tetrahydrofuran with the corresponding potassium salts. The ^{11}B chemical shifts for one of these titrations are shown in Table II.

After the addition of a half equivalent of the potassium salt, the ^{11}B spectrum showed one single band at 31.6 ppm. The intensity of this band increased after addition of one equivalent. This observation allowed the isolation of the compound $UCl_3[HB(3,5\text{-}Me_2Pz)_3]THF$ described above. The I.R. spectra showed the characteristic B–H mode at 2500 cm^{-1}. The stretching vibration $\nu(UCl)$ appears at 280 cm^{-1}

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TABLE I. ^{11}B NMR Spectra Parameters of the Uranium Complexes and Corresponding Potassium Salts.

Sample[a]	δ(ppm)[b]	J(B–H) (ppm)	W(ppm)[c]
$UCl_2[HBPz_3]_2$ (in CH_2Cl_2)	10.0	Unresolv. band	5
$U[HBPz_3]_4$	39.0	Unresolv. band	8
$U[H_2BPz_2]_4THF$	33.2	Unresolv. band	5
$UCl_2[BPz_4]_2$ (in CH_2Cl_2)	42.0	–	1.3
$UCl_3[HB(3,5\text{-}Me_2Pz)_3]THF$	31.6	–	5.5
$UCl_2[HB(3,5\text{-}Me_2Pz)_3]_2$	46.8 34.7 31(sh)	Unresolv. bands	5
$UCl_2[H_2B(3,5\text{-}Me_2Pz)_2]_2THF$	28.6(t)	4.0	5
	–32.4	Unresolv. band	5
$[U[H_2B(3,5\text{-}Me_2Pz)_2]_4$	28.7(t)	4.0	5
KH_2BPz_2	33.2(t)	3.6	2.5
$KHBPz_3$	39.2(d)	4.2	3.0
$KBPz_4$	42.6(s)	–	0.25
$KHB(3,5\text{-}Me_2Pz)_3$	35.4(d)	3.9	3.5
$KIl_2B(3,5\text{-}Me_2Pz)_2$	29.5(t)	3.8	3.0

[a] Samples in THF solution unless otherwise stated. [b] External reference and lock in a glass capillary KBH_4/D_2O. [c] B–H decoupled spectra.

TABLE II. ^{11}B Chemical Shifts of the Titration of UCl_4 with $KHB(3,5\text{-}Me_2Pz)_3$ in THF Solution.

Sample	δ(ppm)
$KHB(3,5\text{-}Me_2Pz)_3$	35.4
$UCl_4 + 0.5\ KHB(3,5\text{-}Me_2Pz)_3$	31.6
$UCl_4 + KHB(3,5\text{-}Me_2Pz)_3$	31.6
$UCl_4 + 2KHB(3,5\text{-}Me_2Pz)_3$	47.5 33.8 31(sh)
$UCl_4 + 4KHB(3,5\text{-}Me_2Pz)_3$	47.5 33.8 31(sh)

External reference and lock KBH_4/D_2O.

TABLE III. ^{11}B Chemical Shifts of the Titration of UCl_4 with $KH_2B(3,5\text{-}Me_2Pz)_2$ in THF Solution.

Sample	δ (ppm)
$KH_2B(3,5\text{-}Me_2Pz)_2$	29.5
$UCl_4 + 0.5KH_2B(3,5\text{-}MePz)_2$	28.3 –32.6
$UCl_4 + KH_2B(3,5\text{-}Me_2Pz)_2$	28.3 –32.6
$UCl_4 + 2KH_2B(3,5\text{-}Me_2Pz)_2$	28.6 –32.8
$UCl_4 + 4KH_2B(3,5\text{-}Me_2Pz)_2$	28.7

External reference and lock KBH_4/D_2O.

(265 cm^{-1} in compound (I)) and another band at 310 cm^{-1} was assigned to a N–U–N mode (325 cm^{-1} in compound (I)). The spectrum changes drastically after the addition of two equivalents, the area of the peak at 31.6 ppm decreasing and new bands appearing at 47.5 and 33.8 ppm. The addition of four equivalents did not cause any visible alteration in the spectra. The spectra obtained on a solution of the solid compound $UCl_2[HB(3,5\text{-}Me_2Pz)_3]_2$ in toluene or tetrahydrofuran displayed the same pattern. The areas of these bands in both cases are different ($A_{\delta 47.5} > A_{\delta 33.8 + \delta 31}$).

The results described above could be explained by reactions of the type:

$$2UCl_2L_2 \rightleftharpoons UCl_3L \cdot x\ thf + UClL_3y\ thf \quad (1)$$

or

$$2UCl_2L_2 \rightleftharpoons UL_4 \cdot x'\ thf + UCl_4 \cdot y'\ thf \quad (2)$$

The second reaction seems improbable as we can obtain similar spectra in toluene and the $UCl_4 \cdot$ y thf species should be insoluble in this solvent.

At the same time the boron spectra indicate the existence of three boron species and this reaction accounts only for two. Moreover the species UL_4 cannot be isolated as a solid compound.

In the equation (1) to the species $UCl_3L \cdot y$ thf could be assigned a chemical shift of 31.6 (species isolated as a solid as referred to above). The two peaks at 47.5 and 33.8 could be assigned respectively to the UCl_2L_2 and $UClL_3$ species, the latter with a chemical shift near the value for the free ligand, as would be expected for a very crowded compound.

Dissolution of the analogous compound $UCl_2[H_2B(3,5\text{-}Me_2Pz)_2]_2$ in THF gave ^{11}B NMR spectra displaying two bands (28.7 and −31.2 ppm). A titration similar to the one described above gave the results shown in Table III.

Unlike the other compound just described, we get from the beginning of the titration two bands in the ^{11}B spectra, except after the addition of 4 equivalents of the ligand where the spectrum displayed only a single line, with a chemical shift near the value for the free ligand (as would be expected for a very crowded compound). The results obtained could be explained in terms of a disproportionation reaction of the type (2) described above. The band with the chemical shift near the value of the free ligand (δ = 28.5) could be assigned to the UL_4 species (this one can be isolated as a solid compound) and the more shifted band to the UCl_2L_2 species (δ = −32.8).

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