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Inorganica Chimica Acta 229 (1995) 315–322

Inorganica Chimica Acta

# Synthesis and structure of tris[dihydrobis(pyrazolyl)borate](tetrahydrofuran)uranium(III), $U[H(\mu\text{-}H)Bpz_2]_3(THF)$: three-center B–H···U(III) interactions in the presence of coordinated THF ligand ☆

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Received 30 June 1994; revised 20 September 1994

**Abstract**

Reaction of $UI_3(THF)_4$ with three equivalents of $KH_2Bpz_2$ gives the complex $U[H(\mu\text{-}H)Bpz_2]_3(THF)$ (**1**). The molecular structure has been determined by single-crystal X-ray diffraction: monoclinic, space group $P2_1/c$, $a=10.662(2)$, $b=13.586(3)$, $c=20.868(6)$ Å, $\beta=103.32(2)°$, $V=2941(1)$ Å$^3$ and $Z=4$. The six nitrogen donor atoms of the chelating $H_2Bpz_2^-$ ligands are arranged in a slightly distorted trigonal prismatic geometry. Two of the $H_2Bpz_2^-$ ligands span triangular edges on a single square face of the trigonal prism, while the third spans the edge common to the remaining two square faces. The oxygen atom of the coordinated THF ligand caps one of the square faces. The remaining two rectangular faces and one of the two triangular faces of the trigonal prism are capped by three-center two-electron B–H···U bridge bonds, providing an effective ten-coordinate U(III) center. The observation of low frequency B–H stretching bands is in accord with the presence of these interactions. In solution the molecule is fluxional. Although the rearrangement is nearly stopped at −100 °C, its nature could not be elucidated. Repeated cycles of dissolution of **1** in toluene and solvent removal yield the THF-free complex $U[H(\mu\text{-}H)Bpz_2]_3$ (**2**). The molecule is also fluxional. The activation energy for equilibration of the $BH_2$ hydrogens is 51 kJ mol$^{-1}$.

*Keywords:* Crystal structures; Uranium complexes; Dihydrobis(pyrazolyl)borate complexes; Agostic BHU interaction

## 1. Introduction

The poly(pyrazolyl)borate ligands provide a flexible and versatile coordination environment for both transition metal ions [1] and the f-elements [2]. For the large f-elements the chemistry has been dominated by the hydrotris(pyrazolyl)borate ligands ($HBpz'_3{}^-$, pz' = substituted pyrazolyl). However, recently a series of interesting complexes with dihydrobis(pyrazolyl)borate ligands has been described. Reger et al. [3] reported the synthesis of $Y[H(\mu\text{-}H)Bpz_2]_3$ and $Y[H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2]_3$ and determined the solid state structure of the former complex. Domingos and co-workers [4] have demonstrated that the complexes $M[H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2]_3$ (M = U, Ce, Sm, Yb) also featured three-center B–H···M bridge type interactions and tricapped trigonal prismatic geometry.

Since steric effect plays a dominant role in determining the coordination number and geometry of f-element complexes it was of interest to determine what effect, if any, the less bulky $H_2Bpz_2^-$ ligand will have on the nature of the tris-chelate U(III) complex. Reported here is the characterization and X-ray structure of the product obtained when $UI_3(THF)_4$ is reacted with three equivalents of $KH_2Bpz_2$.

## 2. Experimental

### 2.1. General procedure

All operations were carried out in a nitrogen-filled Vacuum Atmospheres HE-553-2 DRI LAB or using

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☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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SSDI 0020-1693(94)04260-3

Schlenk techniques in conjunction with a double manifold. Solvents were dried over potassium benzophenone ketyl (THF) or Na/K alloy benzophenone ketyl ($Et_2O$); they were distilled and degassed prior to use. Deuterated solvents were dried over Na/K alloy and distilled.

The ligand $KH_2Bpz_2$ and $UI_3(THF)_4$ were prepared according to published methods [5,6].

IR spectra were recorded on a BOMEM MB-100 FT spectrometer using samples pressed into KBr pellet. NMR spectra were recorded on either a Bruker WH-200 or AM-400 FT spectrometer using flame-sealed tubes. Elemental analysis were performed by the Microanalytical Laboratory, Department of Chemistry, University of Alberta.

### 2.2. Synthesis of $U[H(\mu\text{-}H)Bpz_2]_3(THF)$ (1)

To a slurry of $UI_3(THF)_4$ (183 mg, 0.202 mmol) in THF (4 ml) was added a solution of $KH_2Bpz_2$ (113 mg, 0.606 mmol) in THF (2 ml). The mixture was stirred for 2 h. Inverse filtration through a cannula gave a dark red solution and almost quantitative white precipitate of KI. The THF solvent was removed under vacuum and the residue was washed with hexane (2 ml). Complex **1** was isolated as a dark, almost black solid in 73% yield. Crystals could be obtained by redissolving in $Et_2O$ (4 ml) and cooling the concentrated solution at −40 °C for a few days. IR (KBr, $cm^{-1}$) $\nu$(B–H): 2430, 2283, 2251. $^1H$ NMR (toluene-$d_8$, 23 °C) $\delta$ (ppm): 21.02, 10.01, 9.57 (*H*, pz), 1.67, 0.82 ($CH_2$, THF); $^{11}B$ NMR (toluene-$d_8$, 23 °C) $\delta$ (ppm): −19.2. *Anal.* Calc. for $C_{22}H_{32}N_{12}B_3OU$: C, 35.18; H, 4.29; N, 22.38. Found: C, 35.05; H, 4.55; N, 21.85%.

### 2.3. Synthesis of $U[H(\mu\text{-}H)Bpz_2]_3$ (2)

Complex **1** was dissolved in toluene (1 ml) and the solvent was removed under vacuum, the process was repeated twice. The residue was triturated with hexane (2 ml) and dried under vacuum. Complex **2** was obtained as a black solid in 66% yield. IR (KBr, $cm^{-1}$) $\nu$(B–H): 2432, 2292, 2238. $^1H$ NMR (toluene-$d_8$, 23 °C) $\delta$ (ppm): 22.44, 9.76, 9.60 (*H*, pz); $^{11}B$ NMR (toluene-$d_8$, 23 °C) $\delta$ (ppm): −21.5. *Anal.* Calc. for $C_{18}H_{24}N_{12}B_3U$: C, 31.84; H, 3.56; N, 24.76. Found: C, 32.36; H, 3.44; N, 23.94%.

### 2.4. Variable temperature NMR studies

The studies were carried out on a Bruker AM-400 FT spectrometer using tubes that were flame-sealed under vacuum. Temperature measurements were made with a Bruker B-VT 1000 temperature control unit.

Due to the presence of the paramagnetic U(III) center the $^1H$ chemical shifts are temperature dependent. The chemical shifts of the $\mu$-BH and BH protons of complex **2** in the absence of exchange at the coalescence temperature were calculated from a plot of $\delta$ (ppm) versus $1/T$; $^1H$ NMR (toluene-$d_8$) $\delta$ (ppm): (253 K) 29.31 ($\mu$-BH), 1.10 (BH); (213 K) 33.36 ($\mu$-BH), 1.24 (BH); (203 K) 34.90 ($\mu$-BH), 1.39 (BH); (193 K) 36.65 ($\mu$-BH), 1.59 (BH). The relevant data are: coalescence temperature ($T_c$) 40±10 °C (313 K); $\delta$ (ppm) 24.75 ($\mu$-BH), 0.78 (BH) and $\delta\nu = 9600$ Hz. The free energy of activation based on the formula $\Delta G_c^{\neq} = 1.914 \times 10^{-2}\ T\ [9.972 + \log(T/\delta\nu)]$ kJ $mol^{-1}$ [7] is 51 kJ $mol^{-1}$.

### 2.5. Crystallographic analysis

Single crystals of $U[H(\mu\text{-}H)B(N_2C_3H_3)_2]_3(OC_4H_8)$ (**1**) are, at 20±1 °C, monoclinic, space group $P2_1/c\text{–}C_{2h}^5$ (No. 14) with $a = 10.662(2)$, $b = 13.586(3)$, $c = 20.868(6)$ Å, $\beta = 103.32(2)°$, $V = 2941(1)$ Å$^3$, $Z = 4$ formula units ($D_{calc} = 1.696$ g $cm^{-3}$; $\mu$(Mo K$\bar{\alpha}$) = 5.56 $mm^{-1}$). The computer programs and procedures used for data collection, data reduction, structure solution and refinement of **1** have been reported elsewhere [8]; a summary of the crystallographic data for the present study is given in Table 1. A total of 5396 independent reflections having $2\theta$(Mo K$\bar{\alpha}$) < 50.8° (the equivalent of 0.8 limiting Cu K$\bar{\alpha}$ spheres) was collected on a computer-controlled Nicolet autodiffractometer using full (0.90° wide) $\omega$ scans and graphite-monochromated Mo K$\bar{\alpha}$ radiation. The intensity data were corrected empirically for variable absorption effects using $\psi$ scans for 6 reflections having $2\theta$(Mo K$\bar{\alpha}$) between 8.64 and 25.64°. The structure was solved using 'heavy atom' Patterson techniques with the Siemens SHELXTL-PC software package. The resulting structural parameters have been refined to convergence ($R_1$ (unweighted, based on $F$) = 0.042 for 3311 independent reflections having $2\theta$(Mo K$\bar{\alpha}$) < 50.8° and $I > 3\sigma(I)$) using counter-weighted full-matrix least-squares techniques and a structural model which incorporated anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms. Even though it was possible to locate the hydrogens on all three boron atoms from difference Fourier syntheses and satisfactorily vary their positions in least-squares refinement cycles, their refined positions gave a sufficiently distorted geometry at the borons that it was decided to place the hydrogens at idealized $sp^3$-hybridized positions with a B–H bond length of 1.01 Å and only refine their isotropic thermal parameters. Each hydrogen which is covalently bonded to a carbon was included in the structural model at the fixed idealized $sp^2$ position with a C–H bond length of 0.96 Å and assigned an isotropic thermal parameter which was 1.2 times the equivalent isotropic thermal parameter of its carbon atom.

Table 1
Summary of crystallographic data for $U[H(\mu\text{-}H)B(N_2C_3H_3)_2]_3(OC_4H_8)$ (**1**)

| | |
|---|---|
| Empirical formula | $U[H(\mu\text{-}H)B(N_2C_3H_3)_2]_3(OC_4H_8)$ |
| Color of crystal | black |
| Crystal dimensions (mm) | 0.20×0.43×0.50 |
| Crystal system | monoclinic |
| Space group | $P2_1/c\text{–}C^5_{2h}$ (No. 14) |
| Cell dimensions | |
| $a$ (Å) | 10.662(2) |
| $b$ (Å) | 13.586(3) |
| $c$ (Å) | 20.868(6) |
| $\beta$ (°) | 103.32(2) |
| $Z$ (formula units) | 4 |
| Volume (Å$^3$) | 2941(1) |
| Calculated density (g cm$^{-3}$) | 1.696 |
| Wavelength (Å) | 0.71073 |
| Molecular weight | 751.06 |
| Linear absorption coefficient (mm$^{-1}$) | 5.56 |
| Empirical absorption correction | $\psi$ scans for 6 reflections |
| Range of relative transmission factors | 0.297–1.000 |
| Scan type | $\omega$ |
| Average $\omega$ scan width at half height (°) | 0.38 |
| Scan speed (°/min) | 6.0–3.0 |
| Scan width (°) | 0.90 |
| $2\theta$ Range (°) | 3.0–50.8 |
| Total no. reflections collected | 5564 |
| No. unique reflections | 5396 |
| No. with $I>3\sigma(I)$ | 3311 |
| $R$ (unweighted, based on $F$) | 0.042 |
| $R_w$ (weighted, based on $F$) | 0.049 |
| Data to parameter ratio | 9.2:1 |
| Goodness of fit for the last cycle | 1.100 |
| Largest and mean shift/error | 0.012, 0.000 |
| Largest difference peaks (e$^-$ Å$^{-3}$) (all within 1.04 Å of U atom) | 1.09–0.83 |

## 3. Results and discussion

### 3.1. Synthesis and spectroscopic characterization

Reaction of a slurry of $UI_3(THF)_4$ with three equivalents of $KH_2Bpz_2$ gave $U[H(\mu\text{-}H)Bpz_2]_3(THF)$ (**1**) in good yield, Eq. (1). Complex **1** is a dark, almost black solid, very soluble in THF and toluene, soluble in $Et_2O$, but only sparingly soluble in hexane. Elemental analysis is consistent with the presence of one THF molecule per uranium center. An attempt to remove the THF by heating the compound at 70 °C under dynamic vacuum was unsuccessful, however, repeated cycles of dissolution of **1** in toluene and solvent removal do result in the THF-free complex, $U[H(\mu\text{-}H)Bpz_2]_3$ (**2**).

$$UI_3(THF)_4 + 3KH_2Bpz_2 \xrightarrow[2h]{THF/r.t.} \underset{\mathbf{1}}{U[H(\mu\text{-}H)Bpz_2]_3THF} + 3KI \quad (1)$$

The IR spectrum of **1** in the solid state shows a complex B–H stretching pattern at 2430 and ~2282, 2251 cm$^{-1}$. The higher frequency band can be assigned to a normal terminal B–H stretch, while the bands at lower frequencies are indicative of bridging B–H···U(III) interactions. A similar type of interaction has been described by Domingos and co-workers in $U[H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2]_3$ (**3**), although the shifts in **1** are smaller than those found in the latter complex [4] (B–H···U stretches are at 2270, 2240, 2190, 2090 cm$^{-1}$). We propose that coordination of the THF ligand causes increased steric and electronic saturation of the U(III) center in **1** and weakens the B–H···U interaction. The B–H stretching region of the unsolvated complex $U[H(\mu\text{-}H)Bpz_2]_3$ (**2**) shows a main band at 2432 cm$^{-1}$ (B–H terminal) with a broad multiplet envelope extending down to 2219 cm$^{-1}$. The presence of low frequency features is expected based on the analogous 3,5-dimethylpyrazolyl borate complex **3**. Unfortunately, a comparison between the nature and strength of the agostic B–H···U(III) interactions between complexes **2** and **3** is not possible due to the ill-defined shape of the broad envelope.

The $^1H$ NMR spectrum of **1** shows only one set of signals for the protons of the pyrazolyl rings and one for the THF molecule. The resonances of the latter are shifted from their normal diamagnetic positions and provide further indication for THF coordination. The observation of only one set of resonances is indicative of fluxional behavior. The $^{11}$B NMR spectrum also shows only a single peak, consistent with the $^1$H NMR results. The fluxional nature of **1** was ascertained by a variable temperature $^1$H NMR study. Decoalescence of the signals is observed around −60 °C, but the low temperature limiting spectrum could not be reached even at −100 °C. Thus the mechanism of the rearrangement process remains unknown.

The $^1$H NMR spectrum of complex **2** at room temperature also shows one set of resonances for the pyrazolyl protons (22.44, 9.76 and 9.60 ppm), but contrary to the behavior of complex **3** the BH$_2$ signal could not be detected. In view of this observation and the known fluxional nature of complexes **1** and **3** a variable temperature $^1$H NMR study was carried out (Fig. 1). Interestingly, already at −20 °C two distinct B–H resonances were detected at 29.31 and 1.10 ppm. The signals were assigned to B–H···U(III) bridge and B–H terminals units, respectively, on the basis of the much broadened and more shifted nature of the former signal being under the influence of the paramagnetic U(III) center. Warming the sample to 80 °C resulted in the emergence of a broad averaged BH$_2$ signal at δ 12.7 ppm, a value close to that observed for the averaged BH$_2$ signal in the dimethylpyrazolyl analogue **3** [4]. The lineshape changes are temperature reversible and we calculate a free energy of activation at the coalescence temperature ($T_c$ = 313 K) of 51 kJ mol$^{-1}$ for the process that equilibrates the environments of the two B–H hydrogens. It is interesting to note that Reger et al. [3] reported a very similar energetic barrier for the same process in Y[H(μ-H)Bpz$_2$]$_3$, 47.7 kJ mol$^{-1}$. However in that case the energetics were based on $^{13}$C NMR data of slightly different pyrazolyl rings in the solution ground state structure; the BH$_2$ hydrogens could not be differentiated in this diamagnetic molecule even at low temperature. The observation of well separated B–H signals in **2** for a virtually identical $\Delta G^{\neq}$ is of course due to the paramagnetic U(III) center and represents another interesting example of chemical shift expansion in paramagnetic complexes to the study of fast rate processes [9]. Finally we note that the $^1$H NMR spectrum of U[H(μ-H)B(3,5-Me$_2$pz)$_2$]$_3$ (**3**) showed only one broad BH$_2$ resonance down to 210 K [4]. It thus appears that the agostic B–H···U(III) interactions are stronger in complex **2** than in **3**; this may not be unexpected in view of the more sterically crowded nature of the dimethylpyrazolyl derivative **3**.

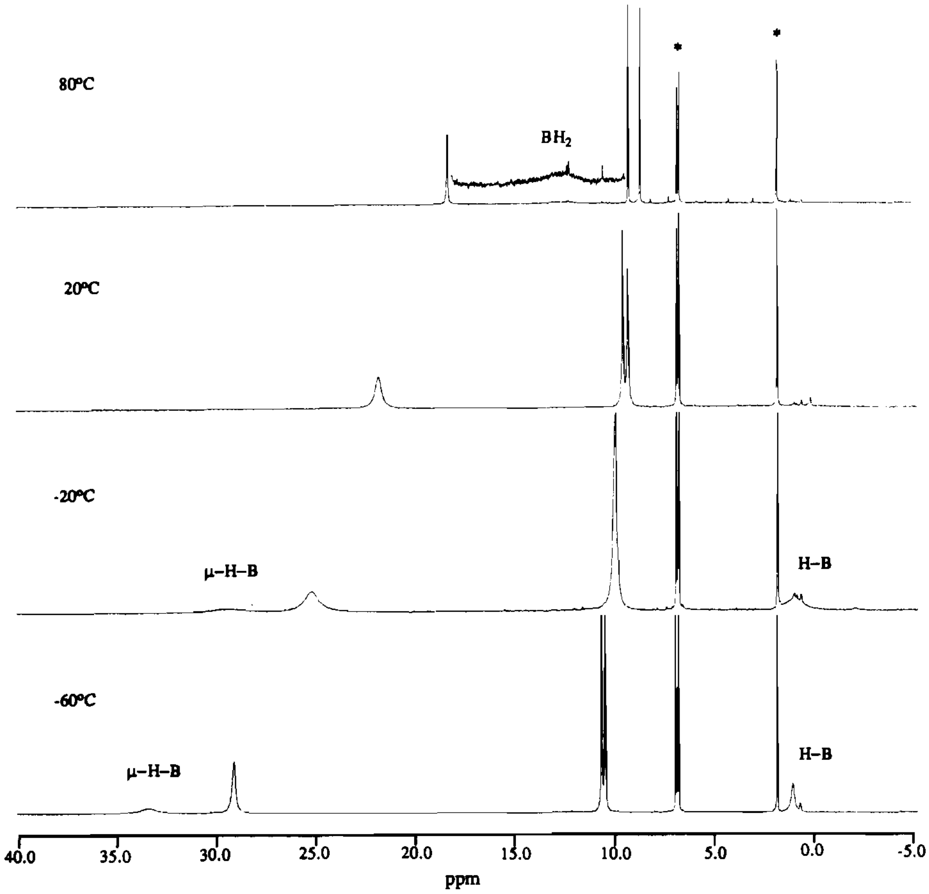

Fig. 1. Variable temperature $^1$H NMR spectra (400 MHz) of U[H(μ-H)Bpz$_2$]$_3$ (**2**) in toluene-d$_8$ (*); the spectrum at −60 °C is $^1$H{$^{11}$B}.

### *3.2. Molecular structure of U[H($\mu$-H)Bpz$_2$]$_3$(THF) (1)*

In order to corroborate the presence of the B–H···U(III) interaction and to determine the precise geometry of the molecule, a single crystal X-ray analysis was performed. The analysis revealed that in the solid state complex **1** is composed of discrete U[H($\mu$-H)Bpz$_2$]$_3$(THF) molecules (Fig. 2) in which each U(III) ion is coordinated to a pair of nitrogens from each of the three bidentate H$_2$Bpz$_2^-$ ligands and the oxygen of a THF ligand. As shown in Fig. 3, the THF oxygen caps one square face of a (necessarily) distorted trigonal prismatic coordination polyhedron described by the six-coordinated nitrogens. The three H$_2$Bpz$_2^-$ ligands span two triangular edges and one square edge of this trigonal prism. The pair of ligands which span the triangular edges occupy opposite sides of a square face not capped by the THF ligand; the third bidentate H$_2$Bpz$_2^-$ ligand spans the vertical edge which is common to the remaining two square faces. Consistent with the solid-state IR data mentioned above, each of the H$_2$Bpz$_2^-$ ligands engages in a three-center two-electron B–H···U agostic bonding interaction by folding along its edge of the coordination polyhedron, buckling the six-membered UN$_4$B ring [10] and tipping the B–H group toward the metal. This results in hydrogen atoms which cap three of the remaining four uncapped faces of the trigonal prism. As shown in Fig. 3, the 'lower' triangular face of the trigonal prism is the only 'uncapped' face. H1bb caps the 'upper' triangular face and H2bb and H3bb cap square faces. U[H($\mu$-H)Bpz$_2$]$_3$(THF) is therefore formally ten-coordinate in the solid state and probably in solution as well. Fractional atomic coordinates for all non-hydrogen atoms of **1** are given with e.s.d.s in Table 2. Selected bond lengths and angles involving non-hydrogen atoms of **1** are given in Table 3. Ligand···ligand contacts on the coordination sphere of crystalline **1** are given in Table 4.

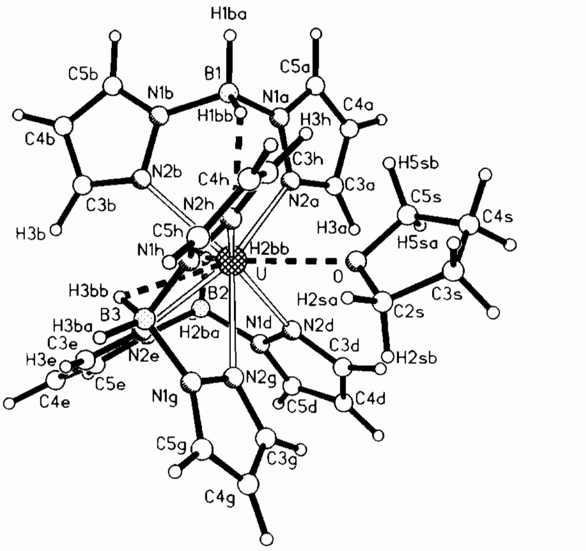

Fig. 2. Perspective drawing of the solid-state structure for U[H($\mu$-H)Bpz$_2$]$_3$(THF) (**1**). For purposes of clarity, uranium atoms are represented by large cross-hatched spheres, oxygen and nitrogen atoms are represented by medium-sized shaded spheres, and carbon and hydrogen atoms are represented by medium-sized and small open spheres, respectively. The U–O and agostic B–H···U bonds are represented by thick dashed lines. C–H and B–H bond lengths at 1.09 and 1.14 Å, respectively, were used to produce this drawing. Selected hydrogen atoms are labeled in this drawing.

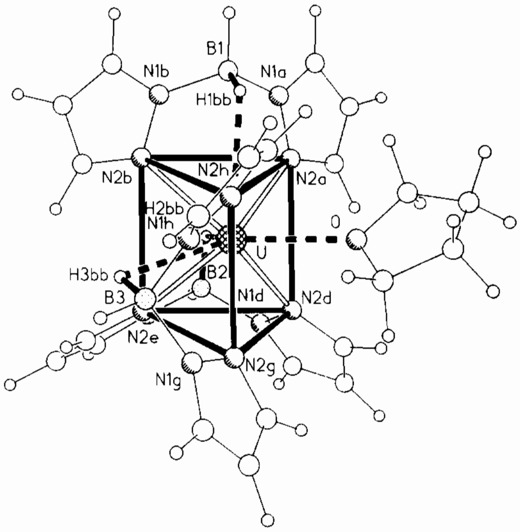

Fig. 3. Perspective drawing of the solid-state structure for U[H($\mu$-H)Bpz$_2$]$_3$(THF) (**1**) with the trigonal prismatic coordination polyhedron included. Ligand atoms are represented as in Fig. 2 and connected with thin-line bonds. The U–O and agostic B–H···U bonds are represented by thick dashed lines.

As shown in Fig. 4, the capped 'square' faces of the trigonal prism are defined by the following three groups of four nearly coplanar nitrogen atoms: I: N2a, N2b, N2d, N2e, coplanar to 0.07 Å; II: N2a, N2d, N2g, N2h, coplanar to 0.08 Å; III: N2b, N2a, N2g, N2h, coplanar to within 0.12 Å. Least-squares mean planes through these 'square' groups of atoms make the following dihedral angles with each other: I–II, 57.9°; I–III, 71.0°; II–III, 51.6°. The triangular faces of the polyhedron are within 3.1° of being parallel. The 'upper' triangle defined by N2a, N2b and N2h makes dihedral angles of 81.4, 85.7 and 85.7° with the mean planes for 'squares' I, II and III, respectively; the 'lower' triangle defined by N2d, N2e and N2g makes dihedral angles of 78.5, 85.1 and 87.7° with them.

The THF oxygen atom is displaced by 1.96 Å out of its 'square' face and capping hydrogen atoms H2bb and H3bb are displaced by 1.81 and 1.75 Å, respectively, out of theirs. H1bb is displaced by 1.66 Å out of the 'upper' triangular face. The U–O bond length is 2.625(8) Å and the U···H distances average 3.00(–, 8, 11, 3) Å. (A fixed B–H bond length of 1.14 Å was used for these calculations.)

Table 2
Atomic coordinates for non-hydrogen atoms in crystalline U[H($\mu$-H)B($N_2C_3H_3$)$_2$]$_3$($OC_4H_8$) (**1**)[a]

| Atom type[b] | Fractional coordinates | | | Equivalent isotropic thermal parameter, $B$[c] (Å$^2$×10) |
|---|---|---|---|---|
| | $10^4x$ | $10^4y$ | $10^4z$ | |
| U | 2419(1) | 2253(1) | 1803(1) | 26(1) |
| B1 | 4421(12) | 1333(11) | 886(8) | 37(4) |
| N1a | 3232(9) | 683(6) | 692(5) | 32(3) |
| N2a | 2202(8) | 873(7) | 938(5) | 33(3) |
| C3a | 1338(11) | 190(8) | 699(7) | 39(3) |
| C4a | 1788(14) | −418(9) | 283(7) | 53(4) |
| C5a | 3007(12) | −97(9) | 288(6) | 41(4) |
| N1b | 4149(9) | 2407(8) | 624(5) | 38(3) |
| N2b | 3470(9) | 3019(7) | 931(5) | 37(3) |
| C3b | 3310(14) | 3867(10) | 574(7) | 49(4) |
| C4b | 3954(16) | 3797(13) | 76(9) | 69(6) |
| C5b | 4399(14) | 2865(12) | 103(7) | 54(4) |
| B2 | −313(13) | 2854(11) | 596(7) | 39(4) |
| N1d | −814(9) | 2205(7) | 1099(5) | 36(3) |
| N2d | 46(8) | 1723(7) | 1588(5) | 37(3) |
| C3d | −661(11) | 1206(9) | 1914(7) | 43(4) |
| C4d | −1962(12) | 1327(10) | 1650(8) | 51(5) |
| C5d | −1996(10) | 1957(9) | 1146(7) | 44(4) |
| N1e | 135(9) | 3830(7) | 919(4) | 35(3) |
| N2e | 1140(8) | 3876(7) | 1451(5) | 36(3) |
| C3e | 1310(11) | 4827(8) | 1626(7) | 43(4) |
| C4e | 419(12) | 5396(9) | 1192(7) | 47(4) |
| C5e | −304(12) | 4750(9) | 771(7) | 43(4) |
| B3 | 3919(15) | 3791(10) | 2999(7) | 43(4) |
| N1g | 2689(10) | 3526(7) | 3222(5) | 39(3) |
| N2g | 1788(10) | 2923(7) | 2853(5) | 42(3) |
| C3g | 858(15) | 2819(10) | 3184(7) | 53(4) |
| C4g | 1152(19) | 3324(13) | 3757(8) | 73(7) |
| C5g | 2293(17) | 3741(11) | 3778(8) | 63(5) |
| N1h | 4847(9) | 2940(7) | 3090(5) | 41(3) |
| N2h | 4617(9) | 2160(7) | 2664(5) | 39(3) |
| C3h | 5560(12) | 1511(9) | 2895(8) | 52(5) |
| C4h | 6392(13) | 1855(12) | 3438(8) | 58(5) |
| C5h | 5906(12) | 2756(11) | 3553(6) | 47(4) |
| O | 2483(8) | 625(6) | 2486(4) | 40(2) |
| C2s | 2672(15) | 605(10) | 3200(8) | 59(5) |
| C3s | 3032(20) | −431(13) | 3381(8) | 85(7) |
| C4s | 2900(29) | −999(12) | 2849(9) | 139(12) |
| C5s | 2628(19) | −356(9) | 2268(9) | 77(6) |
| Idealized BH$_2$ hydrogen positions[d] | | | | |
| H1ba | 5220 | 1003 | 673 | |
| H1bb | 4742 | 1351 | 1446 | |
| H2ba | −1126 | 2989 | 144 | |
| H2bb | 522 | 2471 | 441 | |
| H3ba | 4405 | 4445 | 3298 | |
| H3bb | 3646 | 3989 | 2453 | |

[a] The numbers in parentheses are the e.s.d.s in the last significant digit.

[b] Atoms are labeled in agreement with Figs. 2–4.

[c] This is one-third of the trace of the orthogonalized $B_{ij}$ tensor.

[d] These positions were calculated assuming sp$^3$-hybridization for the boron atom and a B–H bond length of 1.14 Å; they are therefore listed without an e.s.d. Any distances or angles in this paper involving these atoms will be based on these positions.

Table 3
Selected bond lengths (Å) and angles (°) in crystalline U[H($\mu$-H)B($N_2C_3H_3$)$_2$]$_3$($OC_4H_8$) (**1**)[a]

| | | | |
|---|---|---|---|
| Bond lengths (Å) | | | |
| U–N2a[b] | 2.576(10) | U–N2e | 2.607(9) |
| U–N2b | 2.567(11) | U–N2g | 2.601(11) |
| U–N2d | 2.568(9) | U–N2h | 2.608(9) |
| U–O | 2.625(8) | U···H1bb | 3.01[c] |
| | | U···H2bb | 3.10[c] |
| | | U···H3bb | 2.88[c] |
| Bond angles (°) | | | |
| N2aUN2b | 77.4(3) | N2dUN2g | 79.0(3) |
| N2aUN2d | 75.4(3) | N2eUN2g | 73.8(3) |
| N2bUN2d | 124.3(3) | N2aUN2h | 111.6(3) |
| N2aUN2e | 117.5(3) | N2bUN2h | 92.2(3) |
| N2bUN2e | 75.1(3) | N2dUN2h | 143.1(3) |
| N2dUN2e | 76.0(3) | N2eUN2h | 124.3(3) |
| N2aUN2g | 147.8(3) | N2gUN2h | 78.6(3) |
| N2bUN2g | 134.1(3) | | |
| N2aUO | 75.7(3) | N2eUO | 144.3(3) |
| N2bUO | 140.0(3) | N2gUO | 79.4(3) |
| N2dUO | 76.1(3) | N2hUO | 71.2(3) |
| N2aUH1bb | 58.4[c] | N2aUH2bb | 59.5[c] |
| N2bUH1bb | 58.0[c] | N2bUH2bb | 67.1[c] |
| N2dUH1bb | 132.6[c] | N2dUH2bb | 57.2[c] |
| N2eUH1bb | 133.0[c] | N2eUH2bb | 58.2[c] |
| N2gUH1bb | 137.6[c] | N2gUH2bb | 119.9[c] |
| N2hUH1bb | 59.3[c] | N2hUH2bb | 158.4[c] |
| OUH1bb | 82.6[c] | OUH2bb | 120.6[c] |
| N2aUH3bb | 152.1[c] | N2gUH3bb | 59.6[c] |
| N2bUH3bb | 77.1[c] | N2hUH3bb | 58.4[c] |
| N2dUH3bb | 129.4[c] | OUH3bb | 118.8[c] |
| N2eUH3bb | 65.9[c] | | |
| H1bbUH2bb | 102.3[c] | H1bbUH3bb | 98.0[c] |
| H2bbUH3bb | 118.9[c] | | |
| N1aB1N1b | 111.9(9) | N1dB2N1e | 108.6(11) |
| N1gB3N1h | 111.4(10) | | |

[a] The numbers in parentheses are the e.s.d.s in the last significant digit.

[b] Atoms are labeled in agreement with Figs. 2–4.

[c] This parameter was calculated using the idealized coordinates listed in Table 2 for the BH$_2$ hydrogen atoms. Since these hydrogen atoms were place in fixed positions, this parameter is listed without an e.s.d.

The six U–N bonds in **1** have an average[1] length of 2.588(10, 18, 21, 6) Å which is only 0.012 Å longer than the 2.576(14, 22, 43, 12) Å average length observed in the solid state for the U–N bonds in the two crystallographically-independent molecules of U[H($\mu$−H)B(3,5-Me$_2$pz)$_2$]$_3$ (**3**) [4]. Compound **3** is the non-solvated analogue of **1** that incorporates the sterically more-demanding H$_2$B(3,5-Me$_2$pz)$_2^-$ ligand. The six coordi-

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[1] The first number in parentheses following an average value of a bond length or angle is the root-mean-square e.s.d. of an individual datum. The second and third numbers are the average and maximum deviations from the average value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

Table 4
Ligand···ligand contacts (Å) along edges of the coordination polyhedron for $U[H(\mu\text{-}H)B(N_2C_3H_3)_2]_3(OC_4H_8)$ (1) [a]

| | | | |
|---|---|---|---|
| N2a···N2b | 3.22 | N2d···N2g | 3.29 |
| N2d···N2e | 3.19 | N2e···N2g | 3.13 |
| N2g···N2h | 3.30 | | |
| N2a···N2d | 3.14 | N2a···N2h | 4.29 |
| N2b···N2e | 3.15 | N2b···N2h | 3.73 |
| O···N2a | 3.19 | H2bb···N2a | 2.85 |
| O···N2d | 3.20 | H2bb···N2b | 3.16 |
| O···N2g | 3.34 | H2bb···N2d | 2.75 |
| O···N2h | 3.05 | H2bb···N2e | 2.81 |
| | | H3bb···N2b | 3.40 |
| H1bb···N2a | 2.75 | H3bb···N2e | 2.99 |
| H1bb···N2b | 2.73 | H3bb···N2g | 2.74 |
| H1bb···N2h | 2.80 | H3bb···N2h | 2.69 |

[a] A B–H bond length of 1.14 Å was used for these calculations.

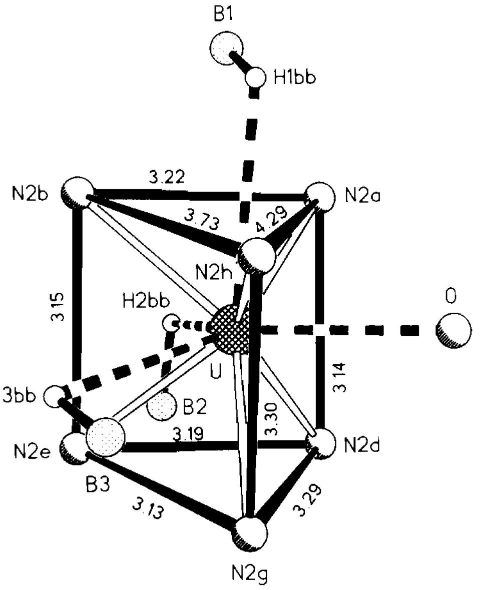

Fig. 4. Perspective drawing of the trigonal prismatic coordination polyhedron observed for U(III) in the solid-state structure of $U[H(\mu\text{-}H)Bpz_2]_3(THF)$ (1). The U–O and agostic B–H···U bonds which cap faces of the polyhedron are represented by thick dashed lines. A B–H bond length of 1.14 Å was used to produce this drawing.

nated nitrogens in 3 also describe a trigonal prism and each of the $H_2B(3,5\text{-}Me_2pz)_2^-$ ligands is involved in three-center two-electron bonding interactions with the metal. The most obvious difference between the U(III) coordination in 3 and 1 is therefore a formal increase by one in coordination number from nine in 3 to ten in 1. A change in coordination number from nine to ten is expected to involve a ~0.05 Å uniform increase in all metal–ligand bond lengths [11]. This does not seem to have occurred in the present case since the U–N bond lengths for 1 and 3 are quite similar. Although this result might loosely be interpreted as indicating that binding a THF ligand to the U(III) ion in $U[H(\mu\text{-}H)Bpz_2]_3$ (2) is sterically equivalent to replacing the hydrogens by methyls at the 3- and 5-positions in each of its six pyrazolyl rings, this would be a gross oversimplification. The U–O distance is similar to the values observed in $[HB(3,5\text{-}Me_2pz)_3]UI_2(THF)_2$ (2.58(1) and 2.65(1) Å) [12], but as expected, longer than the average bond length of 2.52(1) Å in the seven-coordinate $UI_3(THF)_4$ complex [5].

As noted above, the solid-state IR bands associated with the B–H···U interactions are shifted less in 1 than in 3 relative to the normal terminal B–H stretch. This indicates weaker (and longer) three-center agostic U···H–B bonding interactions with the metal in 1. The U···H bridge bonds are indeed weaker in 1 than 3 since the U···B separations average 3.42 Å in 1 and 3.20 Å in 3. The steric and/or electronic differences between 1 and 3 therefore seem to affect the agostic B–H···U bonds much more than the U–N bonds (which were quite similar in the two compounds). This should probably not be surprising since these agostic bonds are the weakest ones to the metal. The steric and/or electronic factors which are responsible for lengthening these weak agostic bonds in 1 relative to 3 should also affect, although probably to a less noticeable degree, the other structural features of 1.

The solid-state structure of 3 has approximate $C_{3h}$ molecular symmetry with the bidentate ligands spanning the three vertical edges between triangular faces of the trigonal prism. This arrangement allows the ligands to pack efficiently by wrapping around the girdle of the trigonal prism with the $BH_2$ of one ligand nestled in between the pyrazolyl rings of the adjacent one. The $BH_2$ group of the $H_2B(3,5\text{-}Me_2pz)_2^-$ ligands can easily move toward the metal in this structure.

If a trigonal prismatic arrangement of six nitrogens is preferred for U(III) in these complexes, a different wrapping pattern must exist for the $H_2Bpz_2^-$ ligands in 1 because of the coordinated THF ligand. Being the largest donor atom of a 'capping' ligand, the THF oxygen will cap a 'square' face of the trigonal prism. Maximum utilization of available agostic B–H···U bonding interactions will then require the capping of a triangular face and consequently the spanning of a triangular edge by at least one $H_2Bpz_2^-$ ligand. This will determine which edges are spanned and which faces are capped by the remaining two ligands.

The data in Tables 3 and 4 reveal two trends which may help our analysis. Three of the six U–N bonds (U–N2e, U–N2g and U–N2h) are systematically longer (av. length 2.605(10, 3, 4, 3) Å) than the other three (av. length 2.570(10, 4, 6, 3) Å) and two edges (N2a···N2h and N2b···N2h) of the trigonal prism are much (>0.40 Å) longer than the others. Both of these effects can be attributed to steric crowding on the coordination sphere which manifests itself in ligand···ligand contacts which are short even after these distortions have occurred. These same interactions should weaken the agostic B–H···U bonds, particularly since two of the face-capping hydrogens (H1bb and H3bb) are directly involved in these short contacts. With B–H and C–H bond lengths of 1.14 and 1.09 Å, respectively, hydrogen atom H1bb is 2.96 Å away from C3h and points directly at it (the B1–H1bb···C3h angle is 177°). Hydrogen atom H3bb is 2.31 Å away from hydrogen atom H3e and 2.91 Å away from C3e. Both of these separations are less than or equal to the respective sums of van der Waals [13] radii: 1.2 Å for hydrogen, 1.5 Å for nitrogen and 1.7 Å for carbon. Interligand H···H, N···H and C···H contacts equal to or less than the van der Waals values of 2.4, 2.7 and 2.9 Å, respectively, also exist between the THF ligand and adjacent pyrazolyl rings: H2sa···C3h, 2.80 Å; H2sa···N2h, 2.68 Å; H2sb···C3g, 2.90 Å; H5sa···C3a, 2.71 Å. Pyrazolyl hydrogen atom H3b is also involved in two short interligand contacts: H3b···N2e at 2.77 Å and H3b···C3e at 2.83 Å. Shortening the three long U–N bonds and/or the two long N···N polyhedral edges would make all of these short contacts even shorter.

Steric factors thus appear to be playing a significant role in weakening the agostic U···H–B bonding interactions in **1** relative to **3**. The U(III) ion in **1** maintains strong bonding interactions with the $H_2Bpz_2^-$ nitrogens and the THF oxygen at the expense of the agostic B–H···U bonds. It is interesting to note that if the total elongation experienced by the agostic U···H bonds (~0.6 Å) on going from **3** to **1** is distributed equally over all ten U···ligand bonds in **1**, a more normal lengthening is observed for the U–N bonds.

## 4. Conclusions

The nature of $U[H(\mu\text{-}H)Bpz_2]_3(THF)$ (**1**) and $U[H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2]_3$ (**3**) complexes underscores the role that steric effects play in the coordination chemistry of the f-elements; use of the sterically less-demanding $H_2Bpz_2^-$ ligands allows THF coordination in **1**. It is noteworthy that with the smaller Y(III) center both ligands give the same tris-chelate complex, $Y[H(\mu\text{-}H)Bpz'_2]_3$. It is also interesting that despite the presence of coordinated THF, complex **1** maintains three agostic B–H···U bonds. Not surprisingly the strength of these interactions is weaker in **1** than in **3**. The coordinated THF ligand is not firmly anchored in complex **1** and the THF-free complex, $U[H(\mu\text{-}H)Bpz_2]_3$ (**2**) is also readily available. This apparent solution lability may allow the synthesis of various $U(H_2Bpz_2)_3(L)$ complexes and a study of the effect of these ligands, steric and electronic, on the strength of the agostic B–H···U bonding.

## 5. Supplementary material

Tables of anisotropic thermal parameters, atomic coordinates for hydrogen atoms, bond lengths and angles involving non-hydrogen atoms, and structure factors have been deposited at the Cambridge Crystallographic Data Center.

## Acknowledgements

We thank the Natural Sciences and Engineering Research Council (Canada), the University of Alberta and Crystalytics Company for financial support of this work.

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