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Synthesis and structure of uranium(III) complexes with dihydrobis(pyrazolyl)borates

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The synthesis of the novel uranium(III) complexes [UI$_2${H$_2$B(3^{t}Bu,5Me-pz)$_2$}(THF)$_2$] **1**, [UI$_2${H$_2$B(3^{t}Bu,5Me-pz)$_2$}(OPPh$_3$)$_2$] **2** (3^{t}Bu,5Me-pz = 3-*tert*-butyl-5-methylpyrazolyl) and [U{Ph$_2$B(pz)$_2$}$_3$] **3** are reported. The molecular structures have been determined by single crystal X-ray diffraction. In monomeric complexes **1** and **2** the U^{III} is seven-co-ordinated by the two pyrazolyl nitrogens, the two iodides and two oxygen atoms of the neutral ligands and by an agostic B–H · · · U interaction. In monomeric **3** the uranium is six-co-ordinated by the nitrogen atoms of the chelating Ph$_2$B(pz)$_2$ ligands which are arranged in a trigonal prismatic geometry around the uranium.

Introduction

Poly(pyrazolyl)borates are very interesting supporting ligands for d- and f-metal centers as their steric and electronic properties can easily be modified by changing the number of pyrazolyl rings co-ordinated to the boron atom and by introducing various sterically bulky pyrazolyl ring substituents.[1–3] For actinides the fine tuning of the co-ordination environment has been dominated by the hydrotris(pyrazolyl)borate ligands [HB(pz*)$_3$, pz* = pyrazolyl or substituted pyrazolyl].[3–6] Previously, we[7] and Takats and co-workers[8] have used dihydrobis(pyrazolyl)borates in trivalent uranium chemistry and the complexes [U{H(μ-H)B(3,5Me$_2$-pz)$_2$}$_3$] (3,5Me$_2$-pz = 3,5-dimethylpyrazolyl) and [U{H(μ-H)B(pz)$_2$}$_3$(THF)] were structurally characterized. Steric effects play a dominant role in determining the co-ordination number and geometry around the metal center and it was of interest to determine what effect replacing the BH$_2$ group with a BPh$_2$ group would have on the nature of the complexes. In addition, the effect of functionalization of the 3 and 5 positions of the pyrazolyl rings with bulky groups, ^{t}Bu and Me, respectively, in the ligand with BH$_2$ groups was examined.

Here we report the synthesis and structural characterization of the monosubstituted complexes [UI$_2${H(μ-H)B(3^{t}Bu,5Me-pz)$_2$}(L)$_2$] (L = THF **1** or OPPh$_3$ **2**) and of the tris-chelate [U{Ph$_2$B(pz)$_2$}$_3$] **3** which have been obtained by treating [UI$_3$(THF)$_4$] with K[H$_2$B(3^{t}Bu,5Me-pz)$_2$] and Na[Ph$_2$B(pz)$_2$], respectively.

Experimental

General procedures

All reactions were carried out under nitrogen, using standard Schlenk and vacuum-line techniques or in an nitrogen-filled glove-box. Solvents were dried and deoxygenated by standard methods and distilled immediately prior to use. Benzene-d$_6$ and toluene-d$_8$ were dried over sodium–benzophenone. Triphenylphosphine oxide was recrystallized from ethyl acetate and vacuum dried. The salts Na[Ph$_2$B(pz)$_2$] and K[H$_2$B(3^{t}Bu,5Me-pz)$_2$] and the complex [UI$_3$(THF)$_4$] were prepared according to published methods.[9–11]

The ^{1}H NMR spectra were recorded on a Varian 300 MHz multinuclear spectrometer, using the chemical shift of the solvent as the internal standard, IR spectra as Nujol mulls on a Perkin-Elmer 577 spectrophotometer and absorption electronic spectra as solutions on a Cary 2390 Varian spectrometer. Carbon, hydrogen and nitrogen analyses were performed on a Perkin-Elmer automatic analyser.

Syntheses

[UI$_2${H(μ-H)B(3^{t}Bu,5Me-pz)$_2$}(THF)$_2$] 1. To a slurry of [UI$_3$(THF)$_4$] (1.8 g, 2 mmol) in THF (20 mL) was slowly added a solution of K[H$_2$B(3^{t}Bu,5Me-pz)$_2$] (653 mg, 2 mmol) in THF. After stirring overnight at room temperature the reaction mixture was centrifuged and the black solution separated. Slow diffusion of *n*-hexane into this black THF solution, during several days, led to the formation of black prismatic crystals, which were separated, washed with *n*-hexane and vacuum dried (1.1 g, 1.2 mmol, 61% yield) (Found: C, 31.1; H, 4.8; N, 5.8. Calc. for C$_{24}$H$_{44}$BI$_2$N$_4$O$_2$U: C, 31.2; H, 4.8; N, 6.1%). IR (cm^{-1}): 2420s, 2280w, 2240w, 2200m, all ν(B–H); 1525s, 1260w, 1240w, 1210w, 1160s, 1120w, 1110w, 1060w, 1010s, ν_{asym}(C–O–C), 980w, 910w, 890m, 880s, 850s, ν_{sym}(C–O–C), 790s, 735s, 730s, 720m, 650m, 630s, 605s, 520m, 465m, 390w, 320w and 300w. ^{1}H NMR: (benzene-d$_6$, 27 °C) δ 12.6 (8 H, br, THF), 9.5 (2 H, br, H(4)), 7.58 (8 H, br, THF), 1.4 (18 H, br, 3-^{t}Bu,), −3.3 (6 H, br, 5-Me) and −15.7 (2 H, vbr, B–H); (toluene-d$_8$, 27 °C) δ 11.2 (8 H, br, THF), 9.6 (2 H, br, H(4)), 6.8 (8 H, br, THF), 1.5 (18 H, br, 3-^{t}Bu,), −3.3 (6 H, br, 5-Me) and −15.7 (2 H, vbr, B–H); (toluene-d$_8$, −50 °C) δ 30.3 (vbr, THF), 23.8 (vbr, THF), 18.1 (vbr, THF), 15.8 (vbr, THF), 14.3 (1 H, H(4)), 7.5 (9 H, 3-^{t}Bu,), 2.8 (1 H, H(4)), −1.8 (9 H, 3-^{t}Bu,), −8.1 (3 H, 5-Me), −10.8 (3 H, 5-Me), −36.6 (1 H, br, B–H) and −66.5 (1 H, vbr, B–H). UV-vis (THF) (λ_{max}/nm): 754w, 904s, 1000s, 1020w, 1040vs, 1070vw, 1170w, 1200s, 1220m and 1240m.

[UI$_2${H(μ-H)B(3^{t}Bu,5Me-pz)$_2$}(OPPh$_3$)$_2$] 2. Addition of OPPh$_3$ (121 mg, 0.43 mmol) to a suspension of complex **1** (200 mg, 0.22 mmol) in toluene (10 cm^3) gave a dark red insoluble solid. The supernatant was removed and the solid washed with *n*-hexane and dried. The dark red solid obtained (200 mg, 0.15 mmol, 70% yield) was formulated as **2**. Dark red crystals suitable for X-ray analysis were obtained by layering hexane on a toluene solution of OPPh$_3$ (42 mg, 0.15 mmol) and layering this on a toluene solution of **1** (70 mg, 0.076 mmol) (Found: C, 47.5; H, 4.5; N, 4.1. Calc. for C$_{52}$H$_{58}$BI$_2$N$_4$O$_2$P$_2$U: C, 47.2; H, 4.3; N, 4.2%). IR (Nujol, cm^{-1}): 2440s, 2280m, 2250w, 2240w, all ν(B–H); 1585s, 1530s, 1480s, 1370s, 1355m, 1135s, 1305w, 1255s, 1235m, 1200m, 1170m, 1155m, 1145s, 1115s, 1095m, 1080m, 1070s, 1020s, 1010m, 990s, 970w, 920w, 890s, 790w, 780s, 750s, 720s, 690s, 550s and 460w. UV-vis (THF) (λ_{max}/nm): 752w, 904s, 1010m, 1070m, 1200m and 1210m.

[U{Ph$_2$B(pz)$_2$}$_3$] 3. To a slurry of [UI$_3$(THF)$_4$] (328 mg, 0.36 mmol) in THF (20 mL) was slowly added a solution of Na[Ph$_2$B(pz)$_2$] (350 mg, 1.09 mmol) in THF. After stirring overnight at room temperature the reaction mixture was vacuum dried. The solid was extracted with toluene and after centrifugation a dark red solution and a white precipitate of NaI was obtained. Slow diffusion of hexane into the saturated solution of toluene led to prismatic red crystals, which were separated, washed with *n*-hexane and vacuum dried (200 mg, 0.18 mmol, 49% yield) (Found: C, 56.6; H, 4.39; N, 14.4. Calc. for $C_{54}H_{48}B_3N_{12}U$: C, 57.1; H, 4.22; N, 14.8%). IR (Nujol, cm^{-1}): 1491m,1480 (sh), 1270s, 1250 (sh), 1180 (sh), 1170s, 1135m, 1100w, 1050s, 1025 (sh), 970m, 910w, 890w, 880s, 825m, 800m, 770w, 740s, 720s, 700s, 640s, 620s and 330m. UV-vis. (THF, λ_{max}/nm): 920s, 1030w, 1080w, 1180 (sh) and 1230s. ^{1}H NMR (toluene-d$_8$, 27 °C): δ 13.2 (6 H, pz), 6.5 (6 H, pz), 3.2 (6 H, pz), 8.2 (6 H, d, J = 6.6, *o*-H, Ph), 8.1 (6 H, br, Ph), 7.6 (6 H, t, J = 6.9, *m*-H, Ph), 7.5 (6 H, t, J = 7.0, *m*-H, Ph) and 6.9 (6 H, t, J = 6 Hz, *p*-H, Ph).

X-Ray crystallographic analysis

X-Ray data were collected from black crystals of complex **1** (0.20 × 0.10 × 0.09 mm), dark red crystals of **2** (0.49 × 0.43 × 0.27 mm) and from a pink crystal of **3** (0.25 × 0.16 × 0.14 mm). All the crystals were mounted in thin-walled glass capillaries within a nitrogen filled glove-box. Owing to decomposition problems, the crystal of **2** was mounted in Nujol and with solvent of crystallization.

Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo-Kα radiation, using an ω–2θ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $15.4 < 2\theta < 29.1°$ for **1**, $15.3 < 2\theta < 26.9°$ for **2** and $14.9 < 2\theta < 27.7°$ for **3**. The crystal data are summarized in Table 1. The data were corrected[12] for Lorentz-polarization effects, for linear decay (no decay was observed for **1**) and empirically for absorption (ψ scans). The crystal of **2** did not provide a good quality data set (variable half-width of the reflections, and a large decay, 61%, during data collection) but the structure was determined unambiguously, although with less accuracy. The heavy atom positions were located by Patterson methods using SHELXS 86.[13] The remaining atoms were located in successive Fourier-difference maps and refined by least squares on F^2 using SHELXL 93.[14] For all three compounds, solvent of crystallization was located in the lattice, severely disordered: one THF molecule in **1**, and in **2** and **3** two and one and a half toluene molecules per asymmetric unit. All the non-hydrogen atoms were refined with anisotropic thermal motion parameters, except for the phenyl carbon atoms in **2** and the atoms of the solvent molecules. When attempting to refine anisotropically the phenyl carbon atoms in **2** some gave negative thermal parameters and others split positions. The contributions of the hydrogen atoms were included in calculated positions, constrained to ride on their carbon and boron atoms (a fixed B–H bond length of 1.01 Å was used) with group U_{iso} values assigned (for **2** and **3** no hydrogen atoms of the solvent molecules were introduced). The final Fourier-difference syntheses revealed electron densities between +0.98 and −1.16 e Å^{-3} for **1**, 1.96 and −2.14 e Å^{-3} for **2** and 2.13 and −1.01 e Å^{-3} for **3,** near the uranium atom. Atomic scattering factors and anomalous dispersion terms were as in SHELXL 93.[14] The drawings were made with ORTEP II[15] and all the calculations were performed on a 3000 Dec α computer.

CCDC reference number 186/1425.

See http://www.rsc.org/suppdata/dt/1999/2015/ for crystallographic files in .cif format.

Results and discussion

The reaction between [UI$_3$(THF)$_4$][11] and one equivalent of K[H$_2$B(3^{t}Bu,5Me-pz)$_2$] in tetrahydrofuran proceeds readily and gives a very dark solution. The KI formed was separated from this suspension by centrifugation and *n*-hexane added to the supernatant solution leading to black crystals of [UI$_2${H(μ-H)B(3^{t}Bu,5Me-pz)$_2$}(THF)$_2$] **1**. Addition of OPPh$_3$ to a solution of complex **1** in toluene, in the molar ratio 2 : 1, gives an insoluble dark red solid formulated as [UI$_2${H(μ-H)B(3^{t}Bu,5Me-pz)$_2$}(OPPh$_3$)$_2$] **2**. Complex **3** is obtained from [UI$_3$(THF)$_4$] with Na[Ph$_2$B(pz)$_2$] in tetrahydrofuran in the molar ratio 1 : 3. Removal of the solvent, extraction with toluene and addition of *n*-hexane leads to dark red crystals of [U{Ph$_2$B(pz)$_2$}$_3$] **3**. Complexes **1** and **3** are soluble in toluene, benzene and tetrahydrofuran and sparingly soluble in hexane, but **2** is only soluble in tetrahydrofuran in which it decomposes, partially regenerating **1**. Complexes **1** and **3** have been characterized in the solid state and in solution, but **2** cannot be characterized in solution, due to its low solubility in non-co-ordinating solvents.

The IR spectra of complexes **1** and **2** show the absorption bands due to the poly(pyrazolyl)borate, namely one sharp and medium B–H stretching band centered at 2420 and 2440 cm^{-1}, respectively, and a complex group of weak bands between 2280 and 2200 cm^{-1}. The higher frequency bands are most certainly due to normal terminal B–H stretches, while the bands at lower frequency are due to the bridging ν(B–H) · · · U interaction.[7,8,16] This deduction was confirmed in the solid state by X-ray crystallography. The presence of the co-ordinated THF is also clear in the IR of **1** due to the presence of two broad and intense absorption bands at 1010 and 850 cm^{-1}.[11] In the IR spectrum of **2** the presence of one very strong absorption band at 550 cm^{-1}, two strong bands at 690 and at 720 cm^{-1} and a weak band at 1585 cm^{-1} [ν(C=C)] confirms the presence of the triphenylphosphine oxide ligands.[17] In the IR spectrum of **2** also appears a complex group of absorption bands between 1000 and 1170 cm^{-1}, with a profile and intensity much higher than observed in the same region for complex **1**. However, the complexity of the spectrum in this region makes an accurate assignment of the ν(P=O) stretch difficult.

The ^{1}H NMR spectrum of complex **1** in toluene-d$_8$ presents at 27 °C one set of resonances for the dihydrobis(pyrazolyl)-borate and two resonances of equal intensity for the two THF molecules at δ 1.5 (^{t}Bu), −3.3 (Me), 9.6 (H(4)), −15.7 (B–H), 11.2 (THF) and 6.8 (THF) in an area ratio of 18 : 6 : 2 : 2 : 8 : 8. Addition of THF to this solution shifts the two resonances observed at δ 11.2 (THF) and 6.8 (THF) towards the frequencies for free THF, confirming the assignment and indicative of THF exchange. The pattern observed in the spectrum of **1** indicates magnetic equivalence of the pyrazolyl rings, of the two B–H protons and of the THF molecules co-ordinated to the metal center, which is not in agreement with the C_1 symmetry found in the solid state. This indicates that some dynamic process is occurring in solution, which is common in complexes of f-elements with poly(pyrazoly)borates.[3,4,18] By lowering the temperature, it was possible to slow down the dynamic process and the spectrum obtained at −50 °C is consistent with the solid state structure, presenting four resonances for the protons of the THF molecules, two distinct sets of resonances for the two magnetically different pyrazolyl rings and two resonances of equal intensity for the protons co-ordinated to the boron atom (see Experimental section). The assignment of the resonances due to the pyrazolyl protons was based on their intensities and

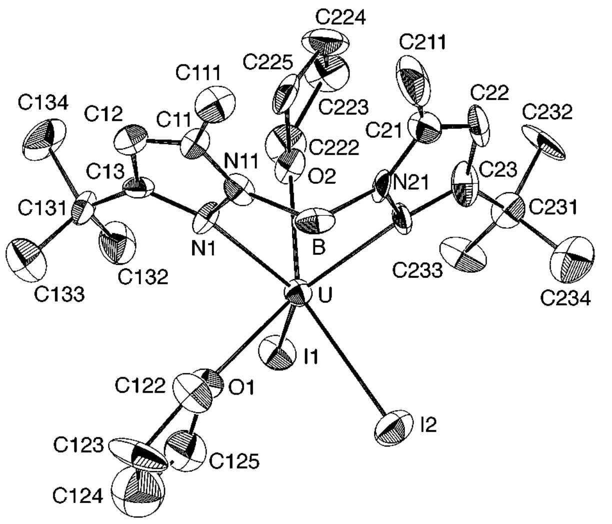

Fig. 1 An ORTEP drawing of complex **1** with atom numbering scheme. Thermal ellipsoids are drawn at the 40% probability level.

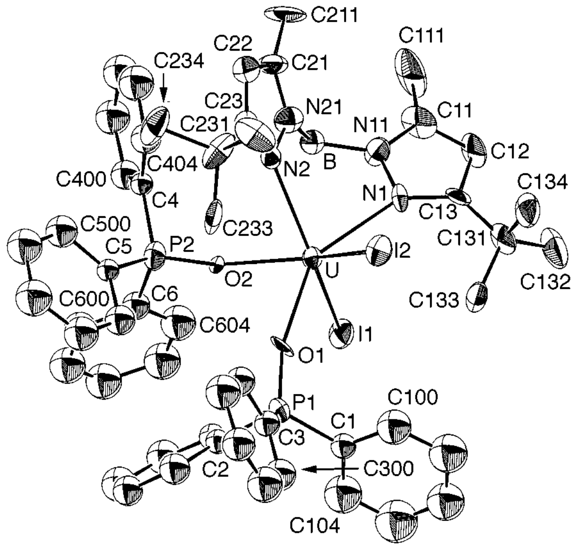

Fig. 2 An ORTEP drawing of complex **2**. Details as in Fig. 1.

the resonances due to the B–H protons were assigned based on their form. The two signals observed at −50 °C at δ −66.5 and −36.6 were assigned to B–H···U bridge and B–H terminal units, respectively, since the former is much broadened, certainly because of the influence of the paramagnetic uranium(III) center.

The ^{1}H NMR spectrum of complex **3** has one set of three broad resonances at δ 13.2 (6 H), 6.5 (6 H) and 3.2 (6 H) for the protons of the pyrazolyl rings. The protons of the phenyl groups appear as five resonances integrating for six protons each at δ 8.2, 8.1, 7.6, 7.5 and 6.9 (see Experimental section). The pattern indicates the magnetic equivalence of the pyrazolyl rings and the non-equivalence of the two individual phenyl groups on each boron atom. The observation of only five resonances, instead of six, for the phenyl groups is because the *p*-H protons of the two phenyl groups are accidentally degenerate. The pattern obtained is consistent with the structure found in the solid state and indicates therefore a rigid behaviour for the molecule at room temperature in solution.

Molecular structures of $[UI_2\{H(\mu\text{-}H)B(3^tBu,5Me\text{-}pz)_2\}(THF)_2]$ 1 and $[UI_2\{H(\mu\text{-}H)B(3^tBu,5Me\text{-}pz)_2\}(OPPh_3)_2]$ 2

The ORTEP drawings of $[UI_2\{H(\mu\text{-}H)B(3^tBu,5Me\text{-}pz)_2\}(THF)_2]$ **1** and $[UI_2\{H(\mu\text{-}H)B(3^tBu,5Me\text{-}pz)_2\}(OPPh_3)_2]$ **2** are shown in Figs. 1 and 2. Selected bond distances and angles are presented in Tables 2 and 3, respectively. In **1** and **2** the uranium atom is seven-co-ordinated by the two pyrazolyl nitrogens, by an agostic B–H···U interaction, by two iodides and by two oxygen atoms of the neutral ligands. Not surprisingly, due to the different nature of the ligands and also due to the tridentate bonding of the dihydrobis(pyrazolyl)borate ligand, the co-ordination geometry is not regular and assignment to one of the common seven-co-ordinate polyhedra (capped octahedron, monocapped trigonal prism and pentagonal bipyramid) is difficult. Related seven-co-ordinated uranium(III) complexes are $[UI_2\{HB(3,5Me_2\text{-}pz)_3\}(THF)_2]$, $[UI\{HB(3,5Me_2\text{-}pz)_3\}_2]$, $[U\{HB(3,5Me_2\text{-}pz)_3\}_2(THF)]^+$ and $[UI_3(THF)_4]$.[4,5,11,19] The complexes stabilized by the hydrotris(pyrazolyl)borate ligand display distorted capped octahedral geometries, but the triiodide displays a pentagonal bipyramidal geometry. Capped octahedral is also the co-ordination geometry that better describes the environment around the U^{IV} in the seven-co-ordinated complexes $[UCl_3\{HB(3,5Me_2\text{-}pz)_3\}(THF)]$, $[UCl_3\{HB(3,5Me_2\text{-}pz)_3\}\{OP(OEt)_3\}]$ and $[UCl(OC_6H_5)_2\text{-}\{HB(3,5Me_2\text{-}pz)_3\}(THF)]$.[20–22] Apparently, the face capping nature of the η^3-hydrotris(pyrazolyl)borate ligand and the presence of the methyl groups on the 3 position seems to impose a more or less distorted capped octahedral geometry. Another common feature of all the seven-co-ordinated complexes of U^{III} and U^{IV} with one hydrotris(pyrazoly)borate is that the (pyrazolyl)borate is tridentate and the nitrogen atoms define one triangular face which is *trans* to the capped site.

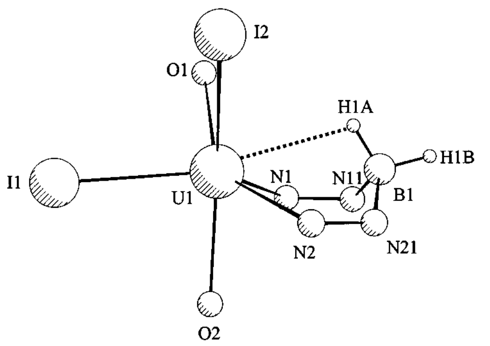

Fig. 3 View of complex **1** emphasizing the conformation of the UN_4B chelate ring and the B–H···U agostic interaction; all the carbon atoms are omitted for clarity.

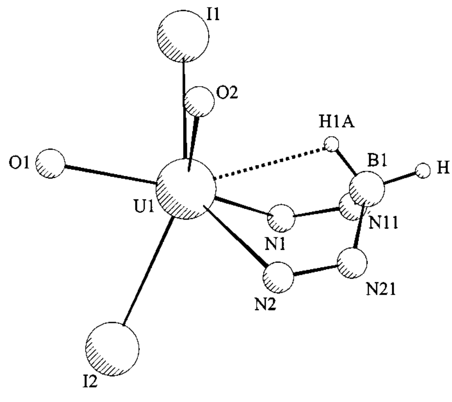

Fig. 4 View of complex **2** as in Fig. 3.

By analogy with other uranium complexes with one poly(pyrazolyl)borate ligand, specifically $[UI_2\{HB(3,5Me_2\text{-}pz)_3\}(THF)_2]$, $[UCl_3\{HB(3,5Me_2\text{-}pz)_3\}(THF)]$, $[UCl_3\{HB\text{-}(3,5Me_2\text{-}pz)_3\}\{OP(OEt)_3\}]$ and $[UCl(OC_6H_5)_2\{HB(3,5Me_2\text{-}pz)_3\}(THF)]$,[4,20–22] the co-ordination geometry around the metal in **1** and **2** is tentatively defined as capped octahedral. In **1** the two staggered triangular faces are defined by N(1)–N(2)–I(1) and I(2)–O(1)–H(1A), respectively. The N(1)–N(2)–I(1) face is capped by the O(2) atom of one tetrahydrofuran (Figs. 1 and 3). In **2** the staggered triangular faces are defined by N(1)–N(2)–

Table 1 Crystal data for $[UI_2\{H(\mu\text{-}H)B(3^tBu,5Me\text{-}pz)_2\}(THF)_2]\cdot THF$ **1**, $[UI_2\{H(\mu\text{-}H)B(3^tBu,5Me\text{-}pz)_2\}(OPPh_3)_2]\cdot 2C_6H_5Me$ **2** and $[U\{Ph_2B(pz)_2\}_3]\cdot 1.5C_6H_5Me$ **3**

	1	**2**	**3**
Formula	$C_{24}H_{44}BI_2N_4O_2U\cdot C_4H_8O$	$C_{52}H_{58}BI_2N_4O_2P_2U\cdot 2C_7H_8$	$C_{54}H_{48}B_3N_{12}U\cdot 1.5C_7H_8$
M	995.38	1519.87	1273.71
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
a/Å	10.386(1)	17.950(3)	13.565(1)
b/Å	13.115(1)	19.866(3)	15.715(2)
c/Å	26.556(2)	18.793(2)	15.929(2)
α/°			118.957(9)
β/°		96.894(12)	92.650(11)
γ/°			97.36(2)
U/Å^3	3617.3(5)	6653(2)	2923.7(6)
T/K	293	293	293
Z	4	4	2
D_c/g cm^{-3}	1.828	1.517	1.447
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073
μ/mm^{-1}	6.225	3.459	2.828
No. reflections measured	5512	9576	9397
No. unique reflections	5247	9070	8202
$R1$ [$I > 2\sigma(I)$]	0.0724	0.1004	0.0501
$wR2$ [$I > 2\sigma(I)$]	0.1003	0.1902	0.1161

Table 2 Selected bond lengths (Å) and angles (°) for $[UI_2\{H(\mu\text{-}H)B(3^tBu,5Me\text{-}pz)_2\}(THF)_2]\cdot THF$ **1**

U–I(1)	3.104(2)	U–N(2)	2.50(2)
U–I(2)	3.132(2)	U–O(1)	2.51(2)
U–N(1)	2.55(2)	U–O(2)	2.584(12)
U···B	3.19	U···H(1A)	2.79[a]
I(1)–U–I(2)	91.59(6)	I(2)–U–O(2)	148.2(3)
I(1)–U–N(1)	126.7(4)	N(1)–U–N(2)	91.4(6)
I(1)–U–N(2)	128.2(4)	O(1)–U–O(2)	134.6(5)
I(2)–U–N(1)	130.8(4)	N(1)–U–O(1)	74.6(6)
I(2)–U–N(2)	84.6(5)	N(1)–U–O(2)	74.1(5)
I(1)–U–O(1)	89.7(4)	N(2)–U–O(1)	138.2(6)
I(1)–U–O(2)	83.6(4)	N(2)–U–O(2)	74.3(6)
I(2)–U–O(1)	76.5(3)	N(11)–B–N(21)	113(2)
O(2)–U–H(1A)	110.9		

[a] This parameter was calculated using a B–H bond distance of 1.01 Å.

Table 3 Selected bond lengths (Å) and angles (°) for $[UI_2\{H(\mu\text{-}H)B(3^tBu,5Me\text{-}pz)_2\}(OPPh_3)_2]\cdot 2C_6H_5Me$ **2**

U–I(1)	3.164(2)	U–N(2)	2.58(2)
U–I(2)	3.199(2)	U–O(1)	2.36(2)
U–N(1)	2.61(2)	U–O(2)	2.351(14)
P(1)–O(1)	1.50(2)	P(2)–O(2)	1.52(2)
U···B	3.11	U···H(1A)	2.62[a]
I(1)–U–I(2)	129.31(6)	I(2)–U–O(2)	139.5(3)
N(1)–U–N(2)	85.1(6)	N(1)–U–O(1)	145.6(6)
O(1)–U–O(2)	79.6(5)	N(1)–U–O(2)	129.3(6)
I(1)–U–N(1)	80.7(4)	N(2)–U–O(1)	123.0(6)
I(1)–U–N(2)	141.8(5)	N(2)–U–O(2)	79.0(5)
I(1)–U–O(1)	85.8(4)	U–O(1)–P(1)	159.8(10)
I(1)–U–O(2)	83.0(3)	U–O(2)–P(2)	168.7(9)
I(2)–U–N(1)	84.8(4)	O(1)–U–H(1A)	146.2
I(2)–U–N(2)	83.9(5)	I(2)–U–O(1)	79.5(4)

[a] This parameter was calculated using a B–H bond distance of 1.01 Å.

O(1) and I(1)–O(2)–H(1A), with the first face capped by the I(2) atom (Figs. 2 and 4). In both complexes the capped and uncapped triangular faces are not parallel and are inclined by 18.5 and 7.7° for **1** and **2**, respectively. The stereochemistry of a homoleptic ML_7 complex with capped octahedral geometry can be defined by the two spherical angles formed by the metal–ligand vectors and the capping ligand.[23] The calculated parameters are 74.6 and 130.3°.[23] For **1** these parameters are the angles O(2)–U–N(1), O(2)–U–N(2), O(2)–U–I(1), O(2)–U–O(1), O(2)–U–I(2) and O(2)–U–H(1A) which are respectively, 74.1(5), 74.3(6), 83.6(4), 134.6(5), 148.2(3) and 110.9°. For **2** the angles I(2)–U–N(1), I(2)–U–N(2), I(2)–U–O(1), I(2)–U–O(2), I(2)–U–I(1) and I(2)–U–H(1A) are 84.8(4), 83.9(5), 79.5(4), 139.5(3), 129.31(6) and 132.3°, respectively. These angles average to 77.3 and 131.2° for **1** and 82.7 and 133.7° for **2**. Compound **2** experiences the greatest distortion from the regular capped octahedral geometry, and the values found for **2** can only be compared to the values found for the uranium(III) complex $[UI_2\{HB(3,5Me_2\text{-}pz)_3\}(THF)_2]$ (82.1 and 134.8°), also described as capped octahedral.[19] In terms of these parameters, compound **1** is more comparable to the CO geometry in the uranium(IV) complexes $[UCl_3\{HB(3,5Me_2\text{-}pz)_3\}(THF)]$ (74.6, 134.9), $[UCl_3\{HB(3,5Me_2\text{-}pz)_3\}\{OP(OEt)_3\}]$ (75.8, 135.4) and $[UCl(OC_6H_5)_2\{HB(3,5Me_2\text{-}pz)_3\}(THF)]$ (74.2, 135.3).[20–22] Distortions from the ideal capped octhaedral geometry in **1** and **2** are also manifested in both interatomic angles and distances (Tables 2 and 3).

In complex **1** the U–N bond distances are comparable, U–N(1) 2.55(2) and U–N(2) 2.50(2) Å, with a mean value of 2.53(2) Å and the N(1)–U–N(2) bond angle is 91.4(6)°. In complex **2** the average U–N [U–N(1) 2.61(2) and U–N(2) 2.58(2) Å] bond distance and the N(1)–U–N(2) bond angle are 2.60(2) Å and 85.1(6)°, respectively. Comparing these values we can say that in **2** they are, respectively, larger and smaller than in complex **1**. The short B···U distances of 3.19 and 3.11 Å in **1** and **2** indicate a B–H···U interaction, stronger in complex **2** than in **1** (Figs. 3 and 4). This stronger B–H···U and the presence of two bulky $OPPh_3$ ligands in **2** are presumably responsible for the increase in the U–N bond distances and for the decrease in the N–U–N bond angle found in **2**. The agostic interaction observed in both complexes is manifest in a short U···B separation and also in the folding of the six-membered UN_4B ring into a "twisted-boat" conformation (Figs. 3 and 4). The folding of the rings is quite pronounced, with dihedral angles between the UN(1)N(2) and the N(11)BN(21) planes of 86.1 and 74.1°, in **1** and **2**, respectively. The smaller dihedral angle in **2** indicates a greater bending of the ring which enables the B–H bond to approach closer the U atom than in **1**. The distorted nature of the UN_4B rings is also shown in the U–N–N–B torsional angles U–N(1)–N(11)–B, U–N(2)–N(21)–B: **1**, −14 and 22; **2**, 7 and 16°. Agostic interactions involving dihydrobis(pyrazolyl)borates and U^{III} have also been previously observed. For $[U\{H_2B(pz)_2\}_3(THF)]$ (ten-co-ordinated) and $[U\{H_2B(3,5Me_2\text{-}pz)_2\}_3]$ (nine-co-ordinated) the solid state structures indicated three-center agostic U···H–B bonding interactions and U···B separations that average to 3.42 and 3.20 Å, respectively.[7,8] It is difficult to compare these values with the ones found for **1** and **2** and to discuss steric or electronic effects, since the complexes have different co-ordination numbers.

In complex **1** one iodide ligand occupies an axial co-ordination site with a U–I(1) bond distance 3.104(2) Å, while the other iodide lies in the equatorial plane with U–I(2) 3.132(2) Å. In **2** there are also two types of U–I bonds: one occupies the capping position [U–I(2) 3.199(2) Å] and the other lies in the equatorial plane [U–I(1) 3.164(2) Å]. These relatively different bond lengths may be compared to those found in **1**, where a weak B–H···U interaction exists and where the less bulky tetrahydrofuran ligands are co-ordinated. Although the difference between the U–I distances in **1**, **2** and $[UI_3(THF)_4]$[11] makes the averaging somewhat artificial, some trends in U–I distances can be detected by comparing the average values: 3.13(3) ($[UI_3(THF)_4]$) ≈ 3.118(2) (**1**) <3.182(2) Å (**2**). This can be interpreted as showing that a η^3-$\{H_2B(3^tBu,5Me\text{-}pz)_2\}$ ligand occupies somewhat the same space as one iodide and two THF ligands. As referred to above it is clear that replacing two THF molecules by two $OPPh_3$ ligands in **2** causes more congestion around the metal center, resulting in longer U–I and U–N bond distances.

The two THF ligands in complex **1** occupy different positions: one lies in the equatorial position [U–O(1) 2.51(2) Å] and the other is capping the triangular face defined by N(1)–N(2)–I(1) [U–O(2) 2.584(12) Å]. The shorter U–O bond distance compares with the average of 2.52(1) Å found in $[UI_3(THF)_4]$,[11] but the oxygen atom of the THF in the capping site is at a longer distance from the metal. The two co-ordinated THF ligands are in their normal twisted conformation.

In complex **2** the two U–O bond distances are comparable with a mean value of 2.36(2) Å, but are shorter than the U–O [2.389(6) Å] distance found in $[U\{MeC_5H_4\}_3(OPPh_3)]$.[24] This difference is reasonable considering the larger co-ordination number (10) of the cyclopentadienyl complex. The U–O–P bond angles in **2** are relatively different, U–O(1)–P(1) 159.8(10) and U–O(2)–P(2) 168.7(9)°. These values compare with the almost linear angle observed in $[U\{MeC_5H_4\}_3(OPPh_3)]$ (162.8(4)°).[24] The difference of 8.9° observed for the U–O–P angle in the two phosphine oxides in **2** is certainly related to steric reasons. The $O(2)PPh_3$ ligand occupies an equatorial position, as well as the two pyrazolyl rings (Fig. 4). In this complex, as discussed above, there is a strong B–H···U interaction, which results in a buckling of the six-membered UN_4B ring. This buckling causes the 3^tBu group of the pyrazolyl ring to move towards the phosphine ligand and certainly forces the linearization of the U–O(2)–P(2) bond (Fig. 4).

To compare the structural data of complexes **1** and **2** with those of other compounds stabilized by pyrazolylborates of this type is difficult, as these are the only examples known of uranium complexes stabilized by one dihydrobis(pyrazolyl)borate ligand that have been structurally characterized. Solid state structures are only known for complexes of uranium-(IV) and -(III) with one hydrotris(pyrazolyl)borates.[3–5,19]

Molecular structure of $[U\{Ph_2B(pz)_2\}_3]$ 3

Compound **3** in the solid state is composed of discrete $[U\{Ph_2B(pz)_2\}_3]$ molecules. An ORTEP drawing is shown in Fig. 5. Selected bond distances and angles are presented in Table 4. The uranium atom is co-ordinated to a pair of nitrogens from each of the three bidentate $\{Ph_2B(pz)_2\}$ ligands. The six nitrogen donors of the poly(pyrazolyl)borates define a trigonal prismatic co-ordination geometry around the metal center, with the bidentate ligands spanning the three vertical edges between the two triangular faces. The two triangular faces of the prism are defined by N6–N2–N3 and by N1–N4–N5, respectively. These faces are almost parallel and the angle between the planes is 0.4°. The distortion of the trigonal prism is not significant compared to the regular polyhedron of rigorous D_{3h} symmetry. In the related complex $[U\{H_2B(3,5Me_2\text{-}pz)_2\}_3]$[7] the solid state structure has approximate C_{3h} molecular symmetry with the bidentate ligands also spanning the three vertical edges between triangular faces of the trigonal prism. However, for $[U\{H_2B(3,5Me_2\text{-}pz)_2\}_3]$ the angles between the two triangular faces are 2.83 and 2.95° for molecules 1 and 2. These values are larger than the value 0.4° found in **3**, a difference that is certainly due to the presence of U···H–B agostic interactions in $[U\{H_2B(3,5Me_2\text{-}pz)_2\}_3]$ as well as the methyl groups in the 3 and 5 positions of the pyrazolyl rings.

Table 4 Selected bond lengths (Å) and angles (°) for $[U\{Ph_2B(pz)_2\}_3]\cdot 1.5C_6H_5Me$ **3**

U–N(1)	2.518(7)	U–N(4)	2.569(7)
U–N(2)	2.531(6)	U–N(5)	2.497(7)
U–N(3)	2.487(7)	U–N(6)	2.558(7)
N(1)–U–N(2)	73.6(2)	N(2)–U–N(6)	83.0(2)
N(3)–U–N(4)	73.6(2)	N(3)–U–N(5)	128.2(2)
N(5)–U–N(6)	73.2(2)	N(3)–U–N(6)	87.7(2)
N(1)–U–N(3)	132.3(2)	N(4)–U–N(5)	86.7(2)
N(1)–U–N(4)	84.4(2)	N(4)–U–N(6)	135.1(2)
N(1)–U–N(5)	91.0(2)	N(5)–U–N(6)	73.2(2)
N(1)–U–N(6)	134.3(2)	av. N–B–N	108.3(7)
N(2)–U–N(3)	95.1(2)	av. N–B–C	108(1)
N(2)–U–N(4)	137.9(2)	N(2)–U–N(5)	128.2(2)

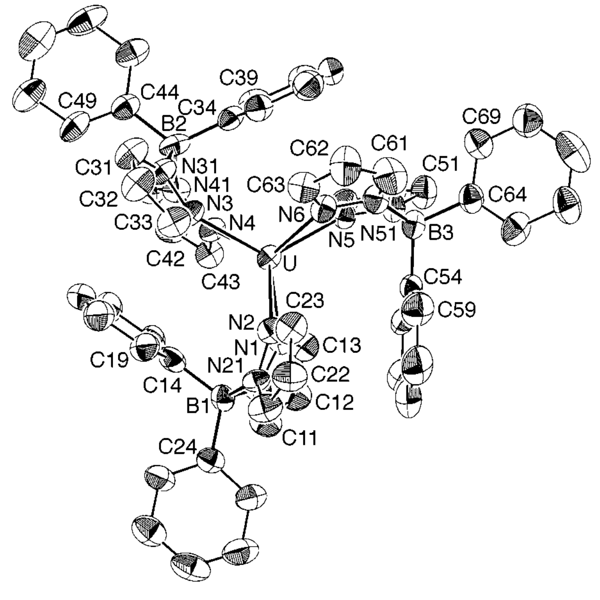

Fig. 5 An ORTEP drawing of complex **3** with atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

In complex **3** there is no interaction between the uranium and the nearest phenyl group, evident from the long bond distances U···B(1), U···B(2), U···B(3) of 3.763, 3.841 and 3.848 Å, respectively. The dihedral angles between the two phenyl groups of each ligand are 72.1, 74.8, and 75.5°, respectively. The U–N bond distances are comparable, with a mean value of 2.53(3) Å. This value is shorter than the average values 2.59(2) and 2.58(3) Å found in the previously characterized analogous $[U\{H_2B(pz)_2\}_3(THF)]$ (ten-co-ordinated) and $[U\{H_2B(3,5Me_2\text{-}pz)_2\}_3]$ (nine-co-ordinated), respectively.[7,8] Complex **3** is six-co-ordinated and this must be the reason why its U–N bond distances are shorter.

Concluding remarks

The use of a bulky dihydrobis(pyrazolyl)borate has allowed the preparation of the first mono-dihydrobis(pyrazolyl)borate uranium(III) complexes, $[UI_2\{H(\mu\text{-}H)B(3^tBu,5Me\text{-}pz)_2\}(THF)_2]$ **1** and $[UI_2\{H(\mu\text{-}H)B(3^tBu,5Me\text{-}pz)_2\}(OPPh_3)_2]$ **2**. The infrared spectra of **1** and **2**, the ^1H NMR static spectra of **1** and the crystal structures of **1** and **2** (short U···B distances and buckling of the six-membered UN_4B chelate ring) are consistent with an agostic B–H···U interaction and indicate a tridentate co-ordination mode of the $\{H_2B(3^tBu,5Me\text{-}pz)_2\}$ ligand in these complexes. A large distortion of the co-ordination geometry is observed due to the symmetry of the ligand and the different nature of the atoms around the metal. This is perhaps the reason why in **1** and **2** the capped face in the capped octahedral geometry is adjacent to the face defined by the η^3-$\{H_2B(3^tBu,5Me\text{-}pz)_2\}$ ligand, and is not *trans*, as observed in the complexes of U^{III} or U^{IV} of the η^3-$\{HB(3,5Me_2\text{-}pz)_3\}$ ligand. By using the diphenylbis(pyrazolyl)borate ligand it was possible to avoid agostic interactions and the six-co-ordinated trigonal prismatic complex $[U\{Ph_2B(pz)_2\}_3]$ was isolated.

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