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Actinide Poly(pyrazol-1-yl)borate Complexes: Synthesis and Structure of Hydrotris(3,5-dimethylpyrazol-1-yl)boratotrichlorotetrahydrofuran Actinide(IV), M[HB(3,5-Me_2Pz)$_3$]Cl_3(THF) (M = Th and U)

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Abstract

The reaction of MCl_4 with K[HB(3,5-Me_2Pz)$_3$] in THF gives the monosubstituted derivatives M[HB(3,5-Me_2Pz)$_3$]Cl_3(THF) (M = Th (**1**) and U (**2**)) in excellent yields. The NMR spectra of the molecules indicate symmetrical structures with equivalent pyrazolyl groups. This has been corroborated by single-crystal X-ray analysis. The uranium center in **2** is seven-coordinate and displays capped octahedral geometry. The tridentate pyrazolylborate moiety and the three Cl atoms define the two staggered triangular faces respectively, the latter is capped by the THF oxygen. The coordination geometry is close to C_{3v} symmetry. The steric congestion imposed by the bulky pyrazolylborate ligand is evidenced by the relative low coordination number and the long U–O bond length, 2.546(4) Å.

Crystal data **2**: monoclinic, $P2_1/n$, $a = 10.195(2)$, $b = 14.905(2)$, $c = 17.414(4)$ Å, $\beta = 100.08(2)^\circ$, $V = 2605.32$ Å^3 and $Z = 4$. Complex **1** is isomorphous with **2**.

Introduction

Compared to the numerous poly(pyrazolyl)borate complexes of the transition metals and the interesting reactivity studies performed thereon [1], the chemistry of the related actinide derivatives is still in its infancy [2]. Although the nature of most actinide poly(pyrazolyl)borates is firmly established on the basis of spectroscopic characterization, the structural deductions have not as yet been supported by X-ray crystallographic studies. This, together with the fact that many of the complexes contain the unsubstituted pyrazole based ligand, H_nBPz_{4-n} (n = 1, 2) and have limited solubility may have hampered further development of this area of chemistry. In view of the often cited analogy between the hydrotris(pyrazolyl)borate ligand and the cyclopentadienyl (C_5H_5) moiety and the spectacular successes obtained by Marks [3] in organoactinide chemistry utilizing the bulky pentamethylcyclopentadienyl (C_5Me_5) ligand, it was of interest to investigate the reaction of the sterically demanding hydrotris (3,5-dimethylpyrazolyl)borate (HB(3,5-Me_2Pz)$_3^-$) ligand with actinides.

We report here the synthesis of M[HB(3,5-Me_2Pz)$_3$]Cl_3(THF) (M = Th (**1**) and U (**2**)) and the first* solid-state structural characterization of an actinide poly(pyrazolyl)borate complex.

Experimental

The preparation and handling of the compounds were carried out under an atmosphere of purified argon or nitrogen using either standard Schlenk techniques in conjunction with a double vacuum-manifold or in an inert atmosphere drybox. All solvents were dried, degassed and distilled just prior to use.

The ligand KHB(3,5-Me_2Pz)$_3$ [5] and the anhydrous halides UCl_4 [6] and $ThCl_4$ [7] were prepared by published methods.

Infrared spectra were recorded on a Nicolet MX-1 FT interferometer or Perkin-Elmer 577 spectrophotometer. NMR spectra were recorded on a Bruker

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*Some preliminary results on compounds **2** and **1** have appeared before [4].

WP-400 (^{1}H and ^{13}C) or SY 80 (^{11}B) Fourier transform spectrometers. Mass spectra were obtained from a AEI MS12 mass spectrometer in conjunction with a Data General Nova 3 computer. Electronic absorption spectra were recorded using a Cary 17 Varian spectrophotometer. Analyses were performed by the analytical services department of the respective institutions.

Preparation of the Complexes

Th[HB(3,5-Me$_2$Pz)$_3$]Cl$_3$(THF)

KHB(3,5-MePz)$_3$ (900.0 mg, 2.68 mmol) in THF (20 cm^3) was added to ThCl$_4$ (1.000 g, 2.68 mmol) in the same solvent (20 cm^3) and stirred overnight. The filtrate from the reaction mixture was evaporated to dryness under vacuum and the resulting oil was triturated with pentane. The supernatant solution was removed and the remaining white solid was dried again under vacuum. Alternatively, the filtrate from the reaction mixture was concentrated under vacuum, n-pentane (*ca.* 20 cm^3) was distilled in and the white solid that precipitated from the solution was filtered off and dried under vacuum. Yields 70–90%. IR spectrum (Nujol mull): ν(B–H) 2550 cm^{-1}, ν(Th–Cl) 258 cm^{-1}. ^{1}H NMR spectrum (δ ppm *versus* TMS); (CDCl$_3$, 25 °C): 2.44, 2.68 (s,s; 3,5-MePz); 5.85 (s; 4-H, Pz); 2.20, 4.68 (m,m; CH$_2$, THF). (C$_6$D$_6$, 25 °C): 1.99, 2.83 (s,s; 3,5-MePz); 5.42 (s; 4H, Pz); 1.41, 4.505 (m,m; CH$_2$, THF), ^{13}C NMR spectrum (CDCl$_3$, 25 °C): 13.04, 14.86 (3,5-MePz); 106.97 (C-4, Pz); 145.22, 151.38 (C-3,5, Pz); 25.67, 72.89 (CH$_2$, THF). ^{11}B NMR spectrum (δ ppm *versus* KBH$_4$): (THF, 25 °C): 33.6 ($w_{1/2}$ 5.9 ppm, J(B–H) 3.1 ppm). (CH$_2$Cl$_2$ 25 °C): 33.7 ($w_{1/2}$ 6.0 ppm). Mass spectrum, (M-THF)$^+$ = 634. *Anal.* Calc. for C$_{19}$H$_{30}$BCl$_3$ON$_6$Th: Th, 32.8; Cl, 15.0; C, 32.2; H, 4.3; N, 11.9. Found: Th, 33.0; Cl, 14.7; C, 32.6; H, 4.9; N, 11.2%.

U[HB(3,5-Me$_2$Pz)$_3$]Cl$_3$(THF)

To a solution of UCl$_4$ (1.117 g, 2.94 mmol) in THF (40 cm^3) was added dropwise a solution of KBH (3,5-Me$_2$Pz)$_3$ (989 mg, 2.94 mmol) in the same solvent (150 cm^3) over 2.5 h. During the addition the color of the solution gradually changed from green to blue–green. Stirring was maintained after the addition for an additional 3 h. The reaction mixture was filtered and the solvent removed under vacuum. The residue was washed with pentane and dried under vacuum to give a pale green powder in 90% yield. To ensure the presence of one molecule of coordinated THF, the material is recrystallized by slow diffusion of n-hexane into a saturated THF solution over a period of days. This procedure produces blue–green crystals of 2 in *ca.* 80% yield, melting point (m.p.) 210–213 °C (dec.). IR spectrum (Nujol mull); ν(B–H) 2560 cm^{-1}, ν(U–Cl) 280 cm^{-1}, ^{1}H NMR spectrum (δ ppm *versus* TMS) (CDCl$_3$, −10 °C): −3.94, 1.86 (s,s; 3,5-MePz); 8.33 (s; 4-H, Pz); 1.23, 1.57 (s,s; CH$_2$, THF). ^{11}B NMR sepctrum (δ ppm *versus* KBH$_4$); (THF, 25 °C): 31.6 ($w_{1/2}$ 5.5 ppm). (CH$_2$Cl$_2$, 25 °C): 44.0 ($w_{1/2}$ 6.6 ppm). Electronic spectrum (λ, nm); (THF solution): 663(s), 668(s), 676(s), 684(s), 1068(m), 1166(s), 1223(m). (CH$_2$Cl$_2$ solution): 663(s), 675(s), 1094(m). Mass spectrum, (M-THF)$^+$ = 640. *Anal.* Calc. for C$_{19}$H$_{30}$BCl$_3$ON$_6$U: U, 33.4; Cl, 14.9; C, 32.0; H, 4.2; N, 11.8. Found: (LNETI) U, 34.0, Cl, 14.8; C, 31.6; H, 4.0; N, 11.9 (U of A) C, 32.5; H, 3.9; N, 11.8%. ^{1}H NMR spectrum of THF free complex, obtained by slow crystallization from CH$_2$Cl$_2$/pentane mixture: U[HB(3,5-Me$_2$Pz)$_3$]Cl$_3$ (CDCl$_3$, −10 °C) −5.65, 3.71 (s,s; 3,5-MePz), 7.71 (s, 4-H, Pz), 12.41 (brs, H–B).

X-ray Structure Determination

A blue–green crystal of the air-sensitive U[HB(3,5-Me$_2$Pz)$_3$]Cl$_3$(THF), obtained by slow diffusion of n-hexane into a saturated THF solution of the complex at room temperature over 1–2 weeks, was sealed into a thin-walled glass capillary under argon and transferred to the goniostat of an Enraf-Nonius CAD4 diffractometer. Diffraction data were collected and processed as described previously [8]. The data were corrected for absorption effects using an empirical correction based on the absorption surface method of Walker and Stuart [9]. The structure was solved using the direct method [10] and Fourier synthesis and refined by full-matrix least-squares techniques*. All non-hydrogen atoms were refined anisotropically and the contributions of the hydrogen atoms were included as fixed isotropic atoms. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources [12]. Table I gives a summary of the crystal data and the intensity collection. Final atomic positional and thermal parameters are listed in Table II.

A white crystal of the analogous thorium complex was similarly mounted in a capillary. Space group determination ($P2_1/n$; a = 10.194(2), b = 14.893(2), c = 17.475(4) Å and β = 99.89(2)°) revealed that the structure of the complex was isomorphous with that of the uranium derivative, as a result full structural determination was not carried out.

Results and Discussion

The reaction between the anhydrous thorium and uranium tetrachlorides and one equivalent of the

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*The computer programs used in this analysis include the Enraf-Nonius Structure Determination Package by B. A. Frenz [11] and several locally written or modified programs.

TABLE I. Crystallographic Data

Compound	$U[HB(3,5\text{-}Me_2Pz)_3]Cl_3(THF)$
Formula	$C_{19}H_{30}BCl_3N_6OU$
Formula weight	713.69
Space group	$P2_1/n$
a (Å)	10.195(2)
b (Å)	14.905(2)
c (Å)	17.414(4)
β (deg)	100.08(2)
V (Å^3)	2605.32
Z	4
D_{calc} (g/cm^3)	1.819
Crystal size (mm)	0.19 × 0.38 × 0.32
Diffractometer	Enraf-Nonius CAD-4F
Temperature (°C)	22
Radiation (incident beam monochromated)	Mo Kα (λ = 0.71073 Å)
Scan mode	$\omega - 2\theta$
2θ limits (deg)	56.00
Number of unique data ($F_o^2 > 3\sigma(F_o^2)$)	4185
μ(Mo Kα) (cm^{-1})	62.40
Range in absorption correction factors	1.3953–0.8021
Number of parameters refined	280
R	0.032
R_w	0.039

bulky pyrazolylborate ligand, $HB(3,5\text{-}Me_2Pz)_3^-$, proceeds readily and gives, after simple work-up, the monosubstituted derivatives in excellent yields, eqn. (1).

$$MCl_4 + KHB(3,5\text{-}Me_2Pz)_3 \xrightarrow[RT]{THF} M[HB(3,5\text{-}Me_2Pz)_3]Cl_3(THF) + KCl \qquad (1)$$

M = Th (**1**), U (**2**)

Although the synthesis proved uneventful with little evidence of side reaction*, the isolation of pure, mono-THF adducts requires some care. Slow crystallization from THF/hexane proved satisfactory for uranium. However slow crystallization from CH_2Cl_2/pentane gave the THF free complex. Other work-up procedures resulted in materials containing variable amounts of THF. Although the THF free thorium complex could not be obtained, the chemical shifts and integrations of the THF ligand resonances clearly depend on the work-up procedure. Thus, if the crude reaction product is extracted into refluxing toluene, the solvent evaporated and the resulting solid washed with n-pentane and vacuum dried, the ^1H NMR spectrum in benzene-d_6 shows peaks at (intensities in parenthesis): 1.99, 2.83 (9H, 9H, 3,5-MePz), 5.42 (3H, 4-H, Pz) and 1.43, 4.43 (2H, 2H; CH_2, THF).

Notwithstanding these problems, elemental analysis and spectroscopic data are in full accord with the molecular formulation of complexes **1** and **2**. In particular the simple NMR spectra, displaying single signals for the pyrazolyl methyl groups, H-4

TABLE II. Positional (×10^3) and Thermal (×10^2) Parameters[a]

Atom	x	y	z	U (Å^2)	Atom	x	y	z	U (Å^2)
U	322.41(2)	193.53(1)	655.41(1)	2.823(5)	C14	334.1(9)	503.6(5)	618.0(5)	5.9(3)
Cl(1)	136.2(2)	211.0(1)	532.5(1)	5.34(6)	C15	462.1(8)	482.0(5)	613.4(4)	5.4(2)
Cl(2)	435.3(2)	36.9(1)	675.5(1)	4.84(5)	C16	123.9(7)	414.2(6)	633.9(6)	7.1(3)
Cl(3)	236.3(2)	254.3(1)	777.7(1)	5.68(6)	C17	577.3(9)	541.5(5)	603.9(6)	7.7(3)
O	136.3(5)	85.6(3)	672.9(3)	5.3(2)	C23	603.0(7)	205.8(4)	807.4(4)	4.1(2)
N11	475.0(5)	391.0(3)	622.9(3)	4.0(2)	C24	727.7(7)	243.0(5)	826.0(4)	4.5(2)
N12	352.1(6)	356.1(4)	630.3(3)	4.2(2)	C25	745.5(7)	294.0(4)	763.0(4)	4.5(2)
N21	633.2(5)	287.9(3)	708.0(3)	3.7(2)	C26	538.1(8)	143.8(6)	856.4(4)	6.0(3)
N22	542.3(5)	233.2(4)	735.7(3)	3.8(2)	C27	863.0(7)	349.1(6)	751.4(5)	6.2(3)
N31	574.5(5)	258.0(4)	562.8(3)	3.5(2)	C33	472.7(6)	147.5(4)	494.0(3)	3.6(2)
N32	465.8(5)	202.8(3)	555.4(3)	3.4(1)	C34	586.2(7)	168.9(5)	463.8(4)	4.2(2)
C1	9.8(8)	115.9(6)	686.6(5)	7.0(3)	C35	648.5(6)	238.2(5)	507.9(3)	3.8(2)
C2	−89(1)	49.0(9)	650.9(9)	13.0(6)	C36	371.1(7)	79.8(5)	466.5(4)	4.4(2)
C3	−16(1)	−31.9(8)	650.1(9)	13.2(6)	C37	779.3(7)	283.1(6)	502.7(5)	6.1(3)
C4	120(1)	−5.0(6)	643.8(6)	8.7(4)	B	598.8(8)	331.5(5)	626.9(5)	3.8(2)
C13	266.5(8)	425.4(5)	627.1(4)	5.2(2)					

[a] The equivalent isotropic thermal parameter is given by: $U = (1/3)(U_{11} + U_{22} + U_{33} + 2U_{23}\cos\alpha + 2U_{13}\cos\beta + 2U_{12}\cos\gamma)$

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*Cleavage of B–N bond in reaction of this ligand with transition metal [13a] and lanthanide halides [13b] has been observed.

and the methylene groups of the coordinated THF ligand indicate a symmetrical structure with equivalent pyrazolyl groups.

In order to corroborate the structural deductions and to provide benchmark parameters for actinide pyrazolylborate complexes the solid state structure of $U[HB(3,5\text{-}Me_2Pz)_3]Cl_3(THF)$ (2) was determined by single crystal X-ray crystallography. As stated the analogous Th complex is isomorphous and is expected to have identical structure and very similar metrical parameters.

The crystal structure consists of well separated, discrete monomeric $U[HB(3,5\text{-}Me_2Pz)_3]Cl_3(THF)$ units. Figure 1 shows a perspective view of the molecular structure and also defines the atomic labelling scheme. Selected bond distances and angles are given in Table III.

The structure represents the first solid state structural characterization of an actidine pyrazolylborate complex and only the third structure determination of a seven-coordinate complex with a non-planar tridentate ligand [14]. The other examples, $Mo(HBPz_3)(CO)_3Br$ [15] and $Ta(HBPz_3)Me_3Cl$ [16], also contain the related unsubstituted hydrotris(pyrazolyl)borate ligand system. The geometry around uranium is best described as capped octahedral

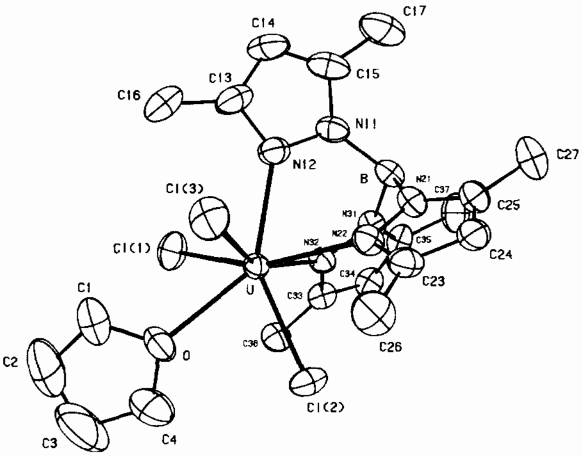

Fig. 1. Molecular structure of $U[HB(3,5\text{-}Me_2Pz)_3]Cl_3$-(THF) and atom numbering scheme. Atoms are represented by thermal ellipsoids at 50% probability level.

TABLE III. Selected Bond Distances (Å) and Angles (deg) for $U[HB(3,5\text{-}Me_2Pz)_3]Cl_3(THF)$

Bond distances					
U–O	2.546(4)	O–C1	1.426(9)		
U–Cl(1)	2.613(2)	O–C4	1.442(9)		
U–Cl(2)	2.599(2)	C1–C2	1.48(1)		
U–Cl(3)	2.603(2)	C2–C3	1.42(2)		
U–N12	2.491(5)	C3–C4	1.46(1)		
U–N22	2.497(5)				
U–N32	2.466(5)				
B–N11	1.534(3)	B–N21	1.538(9)	B–N31	1.551(9)
N11–N12	1.383(7)	N21–N22	1.384(7)	N31–N32	1.369(7)
N11–C15	1.370(8)	N21–C25	1.361(8)	N31–C35	1.351(7)
N12–C13	1.347(8)	N22–C23	1.355(8)	N32–C33	1.362(7)
C13–C14	1.38(1)	C12–C24	1.374(9)	C33–C34	1.389(9)
C14–C15	1.36(1)	C24–C25	1.37(1)	C34–C35	1.374(9)
C13–C16	1.49(1)	C23–C26	1.490(9)	C33–C36	1.466(8)
C15–C17	1.50(1)	C25–C27	1.495(9)	C35–C37	1.509(9)
Bond angles					
Cl(1)–U–Cl(2)	116.16(6)	N12–U–N22	75.1(2)		
Cl(1)–U–Cl(3)	109.53(6)	N12–U–N32	73.5(2)		
Cl(2)–U–Cl(3)	114.00(6)	N22–U–N32	78.3(2)		
O–U–Cl(1)	73.2(1)	Cl(1)–U–N12	81.5(2)		
O–U–Cl(2)	74.8(1)	Cl(1)–U–N22	152.6(1)		
O–U–Cl(3)	75.9(3)	Cl(1)–U–N32	81.5(1)		
O–U–N12	138.8(2)	Cl(2)–U–N12	146.4(1)		
O–U–N22	134.2(2)	Cl(2)–U–N22	78.7(1)		
O–U–N32	131.8(2)	Cl(2)–U–N32	80.9(1)		
N11–B–N22	109.8(5)	Cl(3)–U–N12	82.8(1)		
N11–B–N33	110.4(5)	Cl(3)–U–N22	81.8(1)		
N21–B–N31	110.1(5)	Cl(3)–U–N32	152.2(1)		

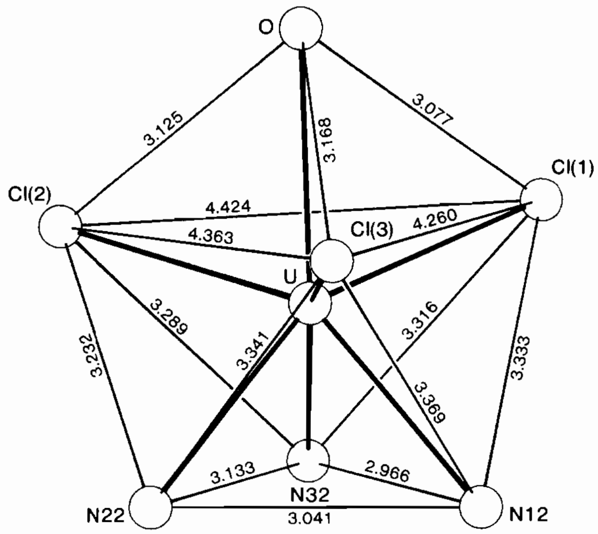

Fig. 2. View of the coordination polyhedron of U[HB(3,5-$Me_2Pz)_3]Cl_3$(THF) showing its capped-octahedral shape. Bond distances and edge lengths are in Å.

(CO, 3:3:1 structure) which represents one of the three basic polytopal forms for seven coordination [14, 17] the other two being the capped trigonal prism (CTP) and pentagonal bipyramid (PB). A clear view of the inner coordination sphere with edge lengths is given in Fig. 2. The tridentate HB(3,5-$Me_2Pz)_3$ moiety occupies one triangular face, while the three chlorine atoms form a staggered triangular face on the other side of the central uranium atom. The staggering of the two faces being enforced by the projection of the three methyl groups of the pyrazolyl rings at C16, C26 and C36 towards the chlorine atoms. The triangular face formed by the latter donors is capped by the ether oxygen of the THF ligand. It is noteworthy that the structure of the Mo complex is not CO but it is based on the four-legged piano stool or 3:4 arrangement of the seven donor atoms. Related $CpML_4$ (Cp = C_5H_5) complexes also adopt a similar geometry [18]. On the other hand, the solid state structure of the high valent tantalum complex is the 3:3:1 CO, resembling the geometry of the uranium compound, **2**. Thus it appears that the 3:4 structure is more suitable for transition metal compounds which exhibit more covalent and thereby directional bonding. Increased electrostatic interactions in the tantalum and even more so in the actinide complexes seems to favor the alternate geometry which, by the way, is predicted to be more stable on the basis of a ligand repulsion model [17b]. Of course the energy differences between the different structural forms need not be large and indeed both the Mo and Ta molecules are fluxional in solution [15, 16].

Within the C_{3v} constraint, the stereochemistry of the 3:3:1 capped octahedron can be defined by the polyhedral edge lengths and by the two spherical angles formed by the metal–ligand vectors and the capping ligand lying on the three-fold axis. In the present context the latter parameters are the O–U–Cl and the O–U–N angles respectively, with observed values of: 73.2(1), 74.8(1), 75.9(1)° and 138.8(2), 134.2(2), 131.8(2)°. These angles average to 74.6 and 134.9° and compare favorably with the predicted values of 74.6 and 130.3° [17b] and with the ones seen in the above mentioned tantalum complex (77.1 and 133.4°). The small increase in the average O–U–N angle from the theoretical expectation indicates a slight compression of the polyhedron toward the poly(pyrazolyl)borate ligand. This is not a surprising observation in view of the rigid nature and the relatively small 'bite' distance offered by this ligand system. The contraction is also reflected in the polyhedral edge lengths. The Kepert predicted ordering [17b], O–Cl > Cl–N > N–N > Cl–Cl, is not seen but, as expected, the N–N distances represent the shortest polyhedral edges. As a final note on the coordination polyhedron it should be noted that it does not have rigorous C_{3v} symmetry. This is evidenced by the modest ranges seen in the values of the shape parameters and by the fact that the planes formed by the three Cl and three N donors are not parallel but are inclined by 4.3°. Nevertheless the distortions are minor and are most probably the result of subtle crystal packing effects.

Bond length comparison with other related complexes is difficult since this is the first structural characterization of an actinide pyrazolylborate compound. However, the U–N bond distances (average 2.49 Å) fall within the range of Yb–N lengths found in $Yb(HBPz_3)_3$ (2.40–2.60 Å) [19] and in $Yb(HBPz_3)_2$(DPM) (where DMP is dipyvaloylmethane) (2.43–2.58 Å) [20]. Comparison with these ytterbium complexes is actually very realistic since the ionic radius of seven-coordinate U(IV) and eight-coordinate Yb(III), seen in the lanthanide complexes, are virtually identical [21]. Not unexpectedly the U–N distances in **2** are longer than those found in amido derivatives of uranium. The average values in some representative examples are: 2.22 Å in $[U(NEt_2)_4]_2$ [22], 2.21 Å in $U_3(CH_3NCH_2CH_2NCH_3)_6$ [23] and 2.27 Å in $U(NPh_2)_4$ [24]. Although the contact nitrogen atoms in both types of complexes is sp^2 hybridized, the smaller effective radius of uranium in the lower coordinate amide complexes combined with the better σ and π donor capacity of the amido nitrogen both contribute toward the reduction of the U–N bond lengths in these compounds. The U–Cl distances (average 2.60 Å) are at the low end of the range of values reported in the 'pseudo-analogous' cyclopentadienyl complexes, 2.56 Å in $U(\eta\text{-}C_5H_4Me)Cl_3(THF)_2$ [25] and 2.65 and 2.66 Å in $U(\eta\text{-}C_5H_5)Cl_3(OPPh_3)$ and $U(\eta\text{-}C_5H_5)Cl_3[OP(NMe_2)_3]_2$

[26], respectively. Not much should be made of these small differences but the trend is consistent with smaller effective radius of uranium as its coordination number is lowered from eight in the cyclopentadienyl complexes to seven in the pyrazolylborate derivative [27]. Contrary to the normal U–N and U–Cl bond lengths, the observed U–O distance at 2.546(4) Å is at least 0.10 Å longer than the similar bond in the previously mentioned cyclopentadienyl complexes and this despite the lower coordination environment of compound 2. This is clearly an indication of the severe steric pressure exercised by the $HB(3,5\text{-}Me_2Pz)_3$ moiety, as is the observation that even the bulky pentamethylcyclopentadienyl ligand can accommodate *two* THF rings in $U[\eta\text{-}C_5Me_5]Cl_3(THF)_2$ [28] as opposed to the presence of only *one* such group in 1 and 2.

The coordinated THF moiety in 2 is in the half-chair ('twisted') conformation. The orientation of the THF oxygen atom upon bonding to a metal has been related to several parameters. These are: the distance of M from the C–O–C plane, the distance of O from the C–M–C plane and the angle between the M–O line and the C–O–C plane [29, 30]. In complex 2 the respective values are: 0.75 and 0.19 Å and 17.2° and show that the oxygen atom is distinctly pyramidal. A correlation has been noted before by Caulton [29] between the pyramidality of oxygen and the M–O bond length. Shorter M–O distances were associated with close to planar THF oxygen donors and vice versa. It was suggested that the π-donor ability of the ether oxygen was responsible for this behaviour. Although the pyramidal nature of the THF oxygen and the long U–O distance in 2 are consistent with this observation, it should be noted that the correlation has not received universal support [30].

Conclusion

In conclusion, straightforward synthesis affords the complexes $M[HB(3,5\text{-}Me_2Pz)_3]Cl_3(THF)$ (M = Th (1) and U (2)) in good yields. As anticipated from the sterically demanding pyrazolylborate ligand, only monosubstituted complexes could be obtained which can only support one molecule of coordinated THF. In fact, the THF in the uranium complex is labile. The structure of complex 2 corroborates the sterically congested nature of the metal center. Preliminary derivatization studies are encouraging and are hopeful signs of extensive chemistry based on the '$M^{IV}[HB(3,5\text{-}MePz)_3]$' moiety [31].

Supplementary Material

Tables of observed and calculated structure factors, anisotropic thermal parameters, derived positional and thermal parameters for hydrogen atoms for complex 2 (35 pages). Copies may be obtained from the author J.T.

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