Journal of the Less-Common Metals, *149* (1989) 271 - 277

ACTINIDE POLY(PYRAZOL-1-YL)BORATE COMPLEXES: SYNTHESIS AND CHARACTERIZATION OF HYDROTRIS(3,5-DIMETHYLPYRAZOL-1-YL)BORATE ACTINIDE(IV) ARYLOXIDES*

A. DOMINGOS, J. MARÇALO, N. MARQUES and A. PIRES DE MATOS

Departamento de Química, ICEN, LNETI, 2686 Sacavém Codex (Portugal)

J. TAKATS

Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2 (Canada)

K. W. BAGNALL

Department of Chemistry, The University of Manchester, Manchester, M13 9PL (U.K.)

(Received June 14, 1988)

Summary

Reactions of $MCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ [M ≡ Th(IV), U(IV)] with NaOAr (Ar ≡ C_6H_5, C_6H_2-2,3,5-Me_3) in thf yielded the complexes $MCl_{3-x}(OAr)_x[HB(3,5\text{-}Me_2Pz)_3](thf)_y$ ($x = 1$ - 3; $y = 0, 1$) which were characterized by IR, near-IR–visible, and ^1H-NMR spectroscopies. The single crystal X-ray structure of $UCl(OC_6H_5)_2$ $[HB(3,5\text{-}Me_2Pz)_3](thf)$ was determined. The uranium centre is seven-coordinate and displays capped octahedral geometry. This structure is compared with the previously reported structure of $UCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$.

1. Introduction

Actinide poly(pyrazolyl)borate chemistry has experienced marked progress since the recent structural characterization of an actinide poly(pyrazolyl)borate complex: $UCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ [1]. Derivatives of this complex and of its thorium analogue with cyclopentadienide, dialkylamides and alkoxides have been described [2, 3], showing a rich chemistry based on the "$M[HB(3,5\text{-}Me_2Pz)_3]$" moiety.

We report here the synthesis and characterization of complexes of the type $MCl_{3-x}(OAr)_x[HB(3,5\text{-}Me_2Pz)_3](thf)_y$ (where M ≡ Th^{IV} and U^{IV} and Ar ≡ C_6H_5 and C_6H_2-2,3,5-Me_3) and the single-crystal X-ray structure determination of $UCl(OC_6H_5)_2[HB(3,5\text{-}Me_2Pz)_3](thf)$.

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*Paper presented at the 18th Rare Earth Research Conference, Lake Geneva, WI, September 12 - 16, 1988.

0022-5088/89/$3.50

2. Experimental details

All preparative work was carried out in a nitrogen-filled glove-box or using Schlenk and vacuum-line techniques. All solvents were dried, degassed and distilled just prior to use.

NaOAr compounds were prepared by reaction of stoichiometric amounts of sodium and the appropriate phenol in thf solution. $MCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ was prepared as reported previously [1].

Electronic absorption spectra were recorded using a Cary 17 Varian spectrophotometer. IR spectra were recorded using a Perkin–Elmer 577 spectrophotometer. NMR spectra were recorded using a Bruker SY80FT multinuclear spectrometer. Carbon, hydrogen and nitrogen analyses were obtained using a Perkin–Elmer automatic analyser.

Tables of analytical and physical data (elemental analyses, IR and electronic spectra), bond distances, bond angles, positional and thermal parameters and observed and calculated structure factors are available from the authors.

2.1. *Syntheses*

All the complexes were prepared in a similar fashion by reaction of $MCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ (approximately 500 mg) with the sodium aryloxides in molar ratios of 1:1, 1:2 or 1:3 in thf solution (20 cm^3). After stirring for 16 h, the solutions were centrifuged. The resulting supernatants were evaporated to dryness and the solid residues were washed with *n*-pentane (2×2 cm^3) and vacuum dried. For $Ar \equiv C_6H_5$ the solids obtained this way were crystallized from thf–*n*-pentane or CH_2Cl_2–*n*-pentane to yield the solvated or unsolvated complexes respectively. Yields were in the range 40% - 70%.

All the compounds gave satisfactory elemental analysis. The IR spectra exhibited the characteristic B–H stretching mode between 2528 and 2550 cm^{-1} (2440 cm^{-1} in $KHB(3,5\text{-}Me_2Pz)_3$) and the M–Cl stretching mode between 246 and 270 cm^{-1}. The electronic spectra of the uranium complexes were identical in thf and CH_2Cl_2 solutions except for the mono and bis phenoxides. In these cases the spectra in thf and CH_2Cl_2 solutions were different due to thf coordination.

2.2. *Crystal data*

Crystals were obtained by slow diffusion of *n*-pentane into a saturated thf solution of the compound. The crystals were triclinic, space group $P\bar{1}$, $a = 10.312(2)$Å, $b = 12.096(4)$Å, $c = 13.934(3)$Å, $\alpha = 80.98(2)°$, $\beta = 80.72(2)°$, $\gamma = 79.57(2)°$, $Z = 2$ and $\mu = 47.4$ cm^{-1} (Mo Kα). Data were collected on a CAD-4 diffractometer (ω - 2θ scan, $2\theta_{max} = 50°$). The structure was solved by Patterson and Fourier methods and full-matrix refinement [4] to $R = 0.054$ and $R_w = 0.047$ for 3248 reflections with $F > 3\sigma(F)$.

3. Results and discussion

Reactions of $MCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ with sodium aryloxides proceed readily and give the appropriate $MCl_{3-x}(OAr)_x[HB(3,5\text{-}Me_2Pz)_3](thf)_y$ complexes in good yields.

For the thorium case the attempted preparation of the monosubstituted complexes ($x = 1$) failed and only the disubstituted derivatives ($x = 2$) were obtained. This has been observed previously with other thorium alkoxides [3] and must be related to the larger thorium(IV) ionic radius compared with that of uranium(IV).

Coordinative unsaturation must also be responsible for the differences observed when $Ar \equiv C_6H_5$ or $C_6H_2\text{-}2,3,5\text{-}Me_3$. In the latter case simple work-up yielded the unsolvated complexes directly, whereas for the smaller unsubstituted phenoxide the isolation of pure products required some care. $UCl_2(OC_6H_5)[HB(3,5\text{-}Me_2Pz)_3](thf)$ was obtained by crystallization from thf–*n*-pentane, but attempts to prepare the unsolvated complex by crystallization from CH_2Cl_2–*n*-pentane failed and led to decomposition.

For the disubstituted case ($x = 2$), both solvated and unsolvated complexes were obtained for thorium and uranium. Both solvated and unsolvated complexes were observed for thorium with $x = 3$, whereas for the smaller uranium(IV) ion only the unsolvated complex was obtained.

Proton NMR data are given in Table 1. Magnetic equivalence of the three pyrazolyl rings was observed for the trisubstituted complexes, whereas for the monosubstituted and disubstituted complexes the spectra indicated that only two of the three pyrazolyl rings were equivalent. These patterns, that have already been found for other $MCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ derivatives [2, 3], were maintained for the solvated complexes as well. This is not unexpected if we assume that the coordination geometry around the metal centre is capped octahedral as was found in $UCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ [1]. Single-crystal X-ray determination of the structure of $UCl(OC_6H_5)_2[HB(3,5\text{-}Me_2Pz)_3](thf)$ was undertaken to corroborate this point. As described below the thf ligand can be considered to occupy the capping position of a distorted capped octahedron.

3.1. *Crystal structure*

The crystal structure consists of discrete molecules in which the uranium atom is seven coordinated by three nitrogens of the tridentate ligand, two oxygens of the phenoxide groups, one chlorine and the oxygen atom of the thf ligand. Figure 1 shows an ORTEP drawing of the molecule.

Not surprisingly, due to the collection of different ligands around uranium, the coordination geometry is not regular and assignment to one of the common seven-coordinate coordination polyhedra (CO, CTP, 3:4 "piano-stool" arrangement) is difficult. However, by analogy with other related pyrazolyl borate complexes [1, 5] and in particular the $UCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ molecule, and due to a definite $N_1N_2N_3$ threefold face, the coordination geometry of uranium is tentatively described as capped octa-

TABLE 1

Room temperature ^{1}H NMR data for aryloxide derivatives of MCl$_3$[HB(3,5-Me$_2$Pz)$_3$](thf)^a

Complex	*3,5-Me$_2$Pz*	*H(4)*	*Other resonances*
UCl$_2$(OC$_6$H$_2$-2,3,5-Me$_3$)[HB(3,5-Me$_2$Pz)$_3$]^b	47.3(3H),19.8(3H)	46.7(1H)	56.3(1H,H-*o*),35.2(3H,CH$_3$-*o*)
	−17.7(6H),−5.2(6H)	−8.3(1H)	24.4(1H,H-*p*),17.4(3H,CH$_3$-*m*),14.7(3H,CH$_3$-*m*)
UCl(OC$_6$H$_2$-2,3,5-Me$_3$)$_2$[HB(3,5-Me$_2$Pz)$_3$]^b	21.9(6H),4.3(6H)	17.5(2H)	20.9(2H,H-*o*),12.4(2H,H-*p*),8.2(6H,CH$_3$-*o*)
	−28.9(3H),−6.2(3H)	−8.1(1H)	6.7(6H,CH$_3$-*m*),6.2(6H,CH$_3$-*m*)
U(OC$_6$H$_2$-2,3,5-Me$_3$)$_3$[HB(3,5-Me$_2$Pz)$_3$]^c	4.62(9H),−1.44(9H)	7.36(3H)	9.32(3H,H-*o*),8.06(3H,H-*p*),2.66(9H,CH$_3$-*m*)
			2.90(9H,CH$_3$-*m*),−0.94(9H,CH$_3$-*o*)
ThCl(OC$_6$H$_2$-2,3,5-Me$_3$)$_2$[HB(3,5-Me$_2$Pz)$_3$]^b	2.43(9H),2.30(3H)	5.70(3H)	6.40(2H,H-*p*),6.03(2H,H-*o*),2.10,2.03(6H,6H,CH$_3$-*m*)
	2.23(6H)		1.80(6H,CH$_3$-*o*)
Th(OC$_6$H$_2$-2,3,5-Me$_3$)$_3$[HB(3,5-Me$_2$Pz)$_3$]^b	2.44(9H),2.23(9H)	5.74(3H)	6.40(3H,H-*p*),6.31(3H,H-*o*),2.15,2.11(9H,9H,CH$_3$-*m*)
			2.04(9H,CH$_3$-*o*)
UCl$_2$(OC$_6$H$_5$)[HB(3,5-Me$_2$Pz)$_3$](thf)^b	56.9(3H),16.4(3H)	46.4(1H)	59.8(2H,H-*o*),31.4(2H,H-*m*),23.6(1H,H-*p*)
	−18.8(6H),−8.6(6H)	−10.5(2H)	−1.5,−2.4(4H,4H,thf)
UCl(OC$_6$H$_5$)$_2$[HB(3,5-Me$_2$Pz)$_3$]^b	19.7(6H),2.6(6H)	16.1(2H)	19.7(4H,H-*o*),13.5(4H,H-*m*),11.3(2H,H-*p*)
	−28.8(3H),−7.1(3H)	−9.0(1H)	
UCl(OC$_6$H$_5$)$_2$[HB(3,5-Me$_2$Pz)$_3$](thf)^b	26.8(6H), 6.0(6H)	16.1(2H)	22.1(4H,H-*o*),14.6(4H,H-*m*),12.1(2H,H-*p*)
	−31.6(3H),−9.4(3H)	−10.8(1H)	3.2,1.5(4H,4H,thf)
U(OC$_6$H$_5$)$_3$[HB(3,5-Me$_2$Pz)$_3$]^c	4.89(9H),−1.72(9H)	6.92(3H)	9.68(6H,d,^3J7Hz,H-*o*),8.83(6H,t,^3J7Hz,H-*m*)
			8.47(3H,t,^3J7Hz,H-*p*)
ThCl(OC$_6$H$_5$)$_2$[HB(3,5-Me$_2$Pz)$_3$]^d	2.48(9H),2.11(9H)	5.51(3H)	6.91(4H,m,H-*m*),6.67(2H,m,H-*p*),6.43(4H,m,H-*o*)
ThCl(OC$_6$H$_5$)$_2$[HB(3,5-Me$_2$Pz)$_3$](thf)^d	2.58(9H),2.08(9H)	5.49(3H)	6.95(4H,m,H-*m*),6.70(2H,m,H-*p*),6.60(4H,m,H-*p*)
			3.92(4H,m,thf),1.47(4H,m,thf)
Th(OC$_6$H$_5$)$_3$[HB(3,5-Me$_2$Pz)$_3$]^d	2.36(9H),2.15(9H)	5.52(3H)	6.94(6H,m,H-*m*),6.68(3H,m,H-*p*),6.46(6H,m,H-*o*)
Th(OC$_6$H$_5$)$_3$[HB(3,5-Me$_2$Pz)$_3$](thf)^d	2.34(9H),2.14(9H)	5.51(3H)	6.97(6H,m,H-*m*),6.69(3H,m,H-*p*),6.50(6H,m,H-*o*)
			4.00(4H,m,thf),1.49(4H,m,thf)

[a] The shifts are in ppm from tetramethylsilane (TMS); downfield shifts are positive; T = 300 K; d = doublet, t = triplet, m = multiplet.

[b] In chloroform-d_1.

[c] In toluene-d_8.

[d] In benzene-d_6.

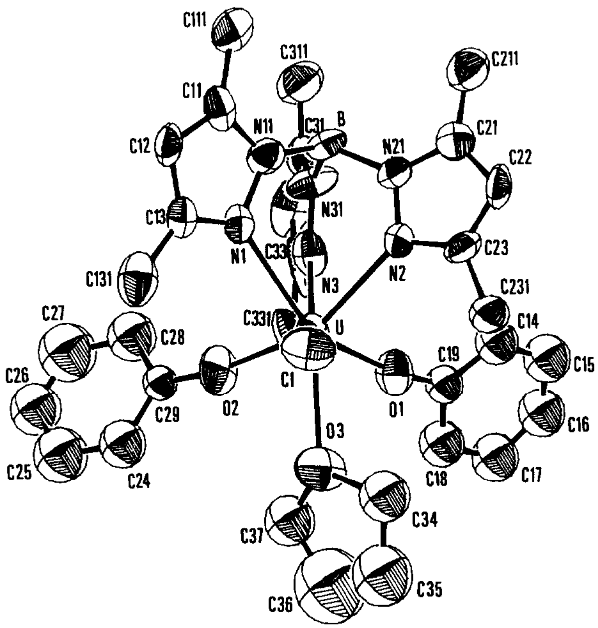

Fig. 1. Molecular structure of $UCl(OC_6H_5)_2[HB(3,5\text{-}Me_2Pz)_3](thf)$ with 50% probability thermal ellipsoids.

hedral. Owing to the presence of different ligands, the extension of the dihedral angle method, described elsewhere [6], was used. The search of the normalized polyhedron for the best threefold face determined by the dihedral angles between the face in question and the three edge-sharing faces, supported the choice of $N_1N_2N_3$ (dihedral angles: 57.8°, 55.2°, 62.4°) and indicated O_3 as the capping atom. The normalized dihedral angles at the edges of the capped face (ClO_1O_2) are as follows: ClO_2, 31.1°, O_1O_2, 26.0° and ClO_1, 5.2°. These can be compared with 24.2°, 24.2° and 24.2° and with 26.7°, 19.1° and 14.6° for the C_{3v} reference polyhedron and for $UCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ respectively. The angles at the metal atom from the capping thf oxygen to the O_1, O_2 and Cl atoms of the capped face are 72.4(3)°, 72.9(4)° and 77.3(4)° respectively, and to the three nitrogen atoms of the uncapped face are 140.4(3)°, 127.3(4)° and 138.1(4)°. The average angles of 74.2° and 135.3° compare with 74.6° and 134.9° reported for $UCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$. The values for ML_7 (CO) are 74.6° and 130.3° [7]. The predicted [7] polyhedral edge length ordering is also reasonably verified; the shortest edges are those from O_3 to O_1, O_2 and Cl and the longest are the edges of the O_1O_2Cl capped face. More regular CO structures have been observed in $UCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ and in the related $Ta(HBPz_3)Me_3Cl$ compound. In fact, in the present structure the dihedral angle at the ClO_1 edge is only 5.2° and the angle formed by the planes of the capped and uncapped faces is 4.9° compared with 0° for the regular CO geometry and with 4.0° in the previously reported uranium complex [1].

TABLE 2

Selected bond distances (Å) and angles (deg)[a]

Bond distances							
U—Cl	2.650(4)	U—N(1)	2.555(11)	O(3)—C(34)	1.52(2)	C(36)—C(35)	1.40(3)
U—O(1)	2.128(9)	U—N(2)	2.475(11)	O(3)—C(37)	1.42(2)	C(37)—C(36)	1.49(3)
U—O(2)	2.116(10)	U—N(3)	2.556(12)	C(35)—C(34)	1.51(2)	O(1)—C(19)	1.32(2)
U—O(3)	2.634(10)	B—N	1.54(1)	C—C	1.37(1)	O(2)—C(29)	1.28(2)
N—N	1.40(1)	N—C	1.33(1)				
Bond angles							
N(2)—U—N(1)	75.7(4)	O(3)—U—N(1)	140.4(4)	N(2)—U—Cl	82.8(3)	O(2)—U—Cl	106.7(4)
N(3)—U—N(1)	72.4(4)	O(3)—U—N(2)	127.3(4)	N(3)—U—Cl	149.4(8)	O(2)—U—N(1)	83.4(4)
N(3)—U—N(2)	76.7(3)	O(3)—U—N(3)	138.1(3)	O(1)—U—Cl	121.1(3)	O(2)—U—N(2)	155.4(3)
O(3)—U—Cl	72.4(3)	C(19)—O(1)—U	169(1)	O(1)—U—N(1)	146.7(5)	O(2)—U—N(3)	84.8(4)
O(3)—U—O(1)	72.9(4)	C(29)—O(2)—U	171(1)	O(1)—U—N(2)	82.2(4)	O(2)—U—O(1)	110.0(4)
O(3)—U—O(2)	77.3(5)	N(1)—U—Cl	80.8(3)	O(1)—U—N(3)	78.5(3)		

[a] The average B—N, N—N, N—C and C—C distances of the ligand HB(3,5Me$_2$Pz)$_3$ are given.

Bond lengths and bond angles are shown in Table 2. A comparison of bond lengths with the structure of $UCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ shows marginally longer U—Cl, U—O_3 and U—N bond distances (respectively 2.650(4) Å, 2.634(10) Å and an average U—N bond distance of 2.53(3) Å compared with 2.60 Å, 2.546 Å and 2.49 Å for $UCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$) due to greater steric congestion from the presence of the bulkier phenoxide groups. In the phenoxide ligands, the U—O bond lengths and U—O—C bond angles average 2.12(1) Å and 170(1)° which are comparable with the values of 2.061(8) Å and 169.2(8)° found in $UCp''_2(Cl)(OC_6H_3\text{-}2,6\text{-}Pr^i_2)$ [8] and with the average U—O bond length observed in $U(OC_6H_5)_4(dmpe)_2$ (2.17(1) Å) [9].

The orientation of the thf oxygen atom on bonding to uranium exhibits the following parameters: distance of U from the C—O—C plane, 0.96 Å; distance of O_3 from the C—U—C plane, 0.23 Å; angle between the U—O_3 line and the C—O—C plane, 21.4°. The higher pyramidal character of the thf oxygen when compared with $UCl_3[HB(3,5\text{-}Me_2Pz)_3](thf)$ is consistent with the longer U—O bond distance in the present structure.

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