Alkoxide and Aryloxide Derivatives of Actinide(IV) Polypyrazolylborates. Part I. Uranium(IV) and Thorium(IV) Hydrotris(3,5-dimethylpyrazol-1-yl)borate Complexes

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Abstract

A series of complexes of the type $M[HB(3,5\text{-}Me_2pz)_3](OR)_xCl_{3-x}$ (with R = Pr^i, Bu^t, C_6H_2-2,4,6-Me_3; $x = 1$, M = U(IV); $x = 2$, M = U(IV), Th(IV); $x = 3$, M = U(IV), Th(IV)) have been prepared from $M[HB(3,5\text{-}Me_2pz)_3]Cl_3(THF)$ and characterized by IR, near IR–Vis, and ^1H NMR spectroscopy. Variable temperature ^1H NMR studies of the uranium compounds indicated restricted rotation of the OR groups; values of $\Delta G^{\ddagger}$ for the rotation about the U–OR bonds were estimated for the complexes $U[HB(3,5\text{-}Me_2pz)_3](OC_6H_2\text{-}2,4,6\text{-}Me_3)Cl_2$ ($\Delta G^{\ddagger} = 49 \pm 4$ kJ mol^{-1}), and $U[HB(3,5\text{-}Me_2pz)_3](OC_6H_2\text{-}2,4,6\text{-}Me_3)_2Cl$ ($\Delta G^{\ddagger} = 41 \pm 3$ kJ mol^{-1}).

Introduction

The synthesis and structure of the complexes $M[HB(3,5\text{-}Me_2pz)_3]Cl_3(THF)$ (M = Th(IV) and U(IV)) have been described recently [1]. Derivatization studies of these complexes with NaCp, $NaN(SiMe_3)_2$ and $KNPh_2$ have also been reported [2]. In this work the reactivity of $M[HB(3,5\text{-}Me_2pz)_3]Cl_3(THF)$ was tested with sodium alkoxides and aryloxides. The results show that an extensive series of complexes can be obtained and a rich chemistry based on the '$M[HB(3,5\text{-}Me_2pz)_3]$' moiety is now emerging.

^1H NMR spectra were obtained for all the compounds and it was observed that variable temperature measurements gave some additional information on the uranium compounds which showed interesting dynamic behaviour. The stereochemical properties of the ligand $HB(3,5\text{-}Me_2pz)_3^-$ makes it a useful ^1H NMR probe because it is quite sensitive to the ligand arrangement around the metal centre and in some cases provides supplementary information about the dynamic behaviour of the other ligands.

Experimental

Materials and Methods

All operations were carried out with exclusion of oxygen and moisture in a nitrogen-filled glove-box or using Schlenk and vacuum-line techniques. THF and toluene were dried by refluxing under nitrogen with Na/K alloy and were distilled prior to use. n-Pentane was dried by fractional distillation from P_2O_5 and stored over Linde type 4A molecular sieves. CH_2Cl_2 was predried with $CaCl_2$, distilled from P_2O_5 and stored over Linde type 4A molecular sieves. All the solvents were degassed several times on the vacuum line before use. Deuterated solvents were dried over Na (toluene, benzene and tetrahydrofuran) or P_2O_5 (chloroform) and distilled.

The complexes $U[HB(3,5\text{-}Me_2pz)_3]Cl_3(THF)$ and $Th[HB(3,5\text{-}Me_2pz)_3]Cl_3(THF)$ were prepared according to the literature procedures [1]. 2,4,6-Trimethylphenol (Aldrich) was purified by sublimation and isopropanol (Merck) and t-butanol (Carlo Erba) were dried by standing over CaH_2 and distilled from CaH_2. Sodium t-butoxide and sodium isopropoxide were prepared by refluxing the appropriate alcohol in THF with the stoichiometric amount of metallic sodium. Sodium 2,4,6-trimethylphenoxide was prepared by reaction of 2,4,6-trimethylphenol with sodium in benzene.

Physical and Analytical Measurements

Infrared spectra were recorded using a Perkin-Elmer 577 spectrophotometer with Nujol mulls sandwiched between CsI plates. Electronic spectra were recorded using a Cary 17 Varian spectrophotometer with samples in solution. Proton NMR spectra were recorded on a Bruker SY80FT multinuclear spectrometer. C, H and N analyses were performed using a Perkin-Elmer automatic analyser.

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Synthesis

U[HB(3,5-Me$_2$pz)$_3$](OBu^t)Cl$_2$ (1)

NaOBu^t (34 mg, 0.35 mmol) in THF (10 ml) was added to a solution of U[HB(3,5-Me$_2$pz)$_3$]Cl$_3$-(THF) (250 mg, 0.35 mmol) in THF (10 ml). After stirring overnight the suspension was centrifuged to remove NaCl. The solution was then evaporated to dryness and the green solid obtained was washed with n-pentane (2 ml) and vacuum dried.

U[HB(3,5-Me$_2$pz)$_3$](OBu^t)$_2$Cl (2a)

U[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (275 mg, 0.39 mmol) and NaOBu^t (75 mg, 0.78 mmol) were stirred together in THF (20 ml) overnight. The solution was centrifuged and then evaporated to dryness. The solid was washed with n-pentane (2 ml) and then extracted into n-pentane (10 ml). Slow evaporation of this solution gave green crystals of the complex.

Th[HB(3,5-Me$_2$pz)$_3$](OBu^t)$_2$Cl (2b)

A colourless microcrystalline solid was obtained in the same way using Th[HB(3,5-Me$_2$pz)$_3$]Cl$_3$-(THF) (355 mg, 0.51 mmol) and NaOBu^t (98 mg, 1.02 mmol).

U[HB(3,5-Me$_2$pz)$_3$](OBu^t)$_3$ (3a)

The green crystalline solid was obtained in a similar way as described for **2a** using U[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (247 mg, 0.35 mmol) and NaOBu^t (101 mg, 1.05 mmol).

Th[HB(3,5-Me$_2$pz)$_3$](OBu^t)$_3$ (3b)

This complex was obtained as a colourless solid by the same procedure, starting from Th[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (265 mg, 0.38 mmol) and NaOBu^t (110 mg, 1.14 mmol).

U[HB(3,5-Me$_2$pz)$_3$](OPr^i)Cl$_2$ (4)

U[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (403 mg, 0.57 mmol) in THF (25 ml) was stirred overnight with NaOPr^i (47 mg, 0.57 mmol). The suspension was centrifuged and the green solution evaporated to dryness. The green solid was recrystallized either from a THF/n-pentane mixture (2 ml/5 ml) or from a CH_2Cl_2/n-pentane mixture (2 ml/5 ml).

U[HB(3,5-Me$_2$pz)$_3$](OPr^i)$_2$Cl (5a)

This complex was prepared in an identical manner, starting from U[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (312 mg, 0.44 mmol) and NaOPr^i (72 mg, 0.88 mmol). The green product was not recrystallized.

Th[HB(3,5-Me$_2$pz)$_3$](OPr^i)$_2$Cl (5b)

The white solid was prepared in the same way from Th[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (398 mg, 0.57 mmol) and NaOPr^i (93 mg, 1.14 mmol).

U[HB(3,5-Me$_2$pz)$_3$](OPr^i)$_3$ (6a)

U[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (354 mg, 0.50 mmol) was stirred overnight with NaOPr^i (123 mg, 1.50 mmol) in THF (20 ml). After centrifuging, the THF solution was evaporated to dryness and the resulting solid extracted into n-pentane (15 ml). Evaporation of the n-pentane gave a green solid which was vacuum dried.

Th[HB(3,5-Me$_2$pz)$_3$](OPr^i)$_3$ (6b)

The white solid was prepared in the same way from Th[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (239 mg, 0.34 mmol) and NaOPr^i (84 mg, 1.02 mmol).

U[HB(3,5-Me$_2$pz)$_3$](OC$_6$H$_2$-2,4,6-Me$_3$)Cl$_2$, (7)

U[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (230 mg, 0.32 mmol) and NaOC$_6$H$_2$-2,4,6-Me$_3$ (51 mg, 0.32 mmol) were stirred overnight in THF (20 ml). The solution was centrifuged to remove NaCl and the THF evaporated under vacuum. The green solid obtained was washed with n-pentane (2 ml) and vacuum dried.

U[HB(3,5-Me$_2$pz)$_3$](OC$_6$H$_2$-2,4,6-Me$_3$)$_2$Cl (8a)

This compound was prepared in the same way in THF (20 ml) from U[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (254 mg, 0.36 mmol) and NaOC$_6$H$_2$-2,4,6-Me$_3$ (113 mg, 0.72 mmol).

Th[HB(3,5-Me$_2$pz)$_3$](OC$_6$H$_2$-2,4,6-Me$_3$)$_2$Cl (8b)

This complex was also prepared, as a white solid, by this method, starting with Th[HB(3,5-Me$_2$pz)$_3$]-Cl$_3$(THF) (204 mg, 0.29 mmol) and NaOC$_6$H$_2$-2,4,6-Me$_3$ (91 mg, 0.58 mmol), using a reaction time of 4 h.

U[HB(3,5-Me$_2$pz)$_3$](OC$_6$H$_2$-2,4,6-Me$_3$)$_3$ (9a)

This derivative was obtained as a green solid in the same way using U[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (210 mg, 0.29 mmol) and NaOC$_6$H$_2$-2,4,6-Me$_3$ (140 mg, 0.89 mmol).

Th[HB(3,5-Me$_2$pz)$_3$](OC$_6$H$_2$-2,4,6-Me$_3$)$_3$ (9b)

This compound was prepared as a white solid in the same way using Th[HB(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) (239 mg, 0.34 mmol) and NaOC$_6$H$_2$-2,4,6-Me$_3$ (160 mg, 1.02 mmol).

The results of the physical and analytical measurements are summarized in Table I (^{1}H NMR data) and Table II (analytical and other physical data).

Results and Discussion

Synthesis and Characterization

The alkoxide and aryloxide derivatives of M[HB-(3,5-Me$_2$pz)$_3$]Cl$_3$(THF) were easily obtained by the metathesis reaction shown in eqn. (1):

TABLE I. Room Temperature ^{1}H NMR Data for Alkoxide and Aryloxide Derivatives of M[HB(3,5-Me_2pz)$_3$]Cl_3(THF)[a]

Complex	HB(3,5-Me_2pz)$_3$			Other resonances
	(3,5-Mepz)		H(4)	
U[HB(3,5-Me_2pz)$_3$](OBu^t)Cl_2[b] (1)	46.2(3H), −31.4(6H),	23.5(3H) −8.9(6H)	53.9(1H) −16.8(2H)	65.7(9H,CH_3)
U[HB(3,5-Me_2pz)$_3$](OBu^t)$_2$Cl[b] (2a)	19.5(6H), −35.4(3H),	2.9(6H) −8.8(3H)	16.3(2H) −12.4(1H)	16.1(18H,CH_3)
Th[HB(3,5-Me_2pz)$_3$](OBu^t)$_2$Cl[c] (2b)	2.72(6H), 2.59(3H)	2.03(9H)	5.41(2H) 5.53(1H)	1.39(18H,CH_3)
U[HB(3,5-Me_2pz)$_3$](OBu^t)$_3$[b] (3a)	7.0(9H),	−2.5(9H)	6.8(3H)	2.71(27H,CH_3)
Th[HB(3,5-Me_2pz)$_3$](OBu^t)$_3$[c] (3b)	2.65(9H),	2.03(9H)	5.56(3H)	1.41(27H,CH_3)
U[HB(3,5-Me_2pz)$_3$](OPr^i)Cl_2[d] (4)	51.2(3H), −27.9(6H),	23.8(3H) −8.5(6H)	55.1(1H) −15.5(2H)	167.1(1H,CH), 66.2(6H,CH_3)
U[HB(3,5-Me_2pz)$_3$](OPr^i)Cl_2[e, f] (4)	86.5(3H), −27.1(6H),	14.5(3H) −13.8(6H)	53.5(1H) −15.2(2H)	181.5(1H,CH), 67.0(6H,CH_3)
U[HB(3,5-Me_2pz)$_3$](OPr^i)$_2$Cl[b] (5a)	23.4(6H), −35.4(3H),	2.5(6H) −9.1(3H)	15.6(2H) −12.4(1H)	53.8(2H,CH), 15.6(12H,CH_3)
Th[HB(3,5-Me_2pz)$_3$](OPr^i)$_2$Cl[c] (5b)	2.70(6H), 2.54(3H)	2.03(9H)	5.45(2H) 5.53(1H)	4.36(2H,s,^3J 6Hz,CH) 1.21(12H,d,^3J 6Hz,CH_3)
U[HB(3,5-Me_2pz)$_3$](OPr^i)$_3$[b] (6a)	6.4(9H),	−2.4(9H)	6.7(3H)	18.3(3H,CH), 1.8(18H,CH_3)
Th[HB(3,5-Me_2pz)$_3$](OPr^i)$_3$[c] (6b)	2.54(9H),	2.08(9H)	5.54(3H)	4.42(3H,s,^3J 6Hz,CH) 1.30(18H,d,^3J 6Hz,CH_3)
U[HB(3,5-Me_2pz)$_3$](OC$_6H_2$-2,4,6-Me_3)Cl_2[d] (7)	45.8(3H), −20.6(6H),	16.7(3H) −7.4(6H)	45.0(1H) −10.4(2H)	30.5(2H,*m*-H), 26.5(6H,*o*-CH_3), 17.8(3H,*p*-CH_3)
U[HB(3,5-Me_2pz)$_3$](OC$_6H_2$-2,4,6-Me_3)$_2$Cl[d] (8a)	23.7(6H), −32.0(3H),	6.7(6H) −8.1(3H)	16.4(2H) −9.4(1H)	14.4(4H,*m*-H), 6.2(12H,*o*-CH_3), 1.8(6H,*p*-CH_3)
Th[HB(3,5-Me_2pz)$_3$](OC$_6H_2$-2,4,6-Me_3)$_2$Cl[d] (8b)	2.37(3H), 2.55(6H)	2.60(9H)	5.94(3H)	6.90(4H,*m*-H), 2.37(6H,*p*-CH_3), 2.19(12H,*o*-CH_3)
U[HB(3,5-Me_2pz)$_3$](OC$_6H_2$-2,4,6-Me_3)$_3$[d] (9a)	6.0(9H),	−2.2(9H)	7.5(3H)	8.3(6H,*m*-H), 2.9(9H,*p*-CH_3) −1.0(18H,*o*-CH_3)
Th[HB(3,5-Me_2pz)$_3$](OC$_6H_2$-2,4,6-Me_3)$_3$[d] (9b)	2.29(9H),	2.64(9H)	5.90(3H)	6.89(6H,*m*-H), 2.37(9H,*p*-CH_3), 2.18(18H,*o*-CH_3)

[a]The shifts are in ppm from TMS; downfield shifts are positive; T = 300 K; d = doublet, s = septet. [b]In toluene-d_8. [c]In benzene-d_6. [d]In chloroform-d_1. [e]In tetrahydrofuran-d_8. [f]The ^{1}H NMR spectrum of 4 was recorded in THF-d_8 because the electronic spectra of the complex in CH_2Cl_2 and in THF showed marked differences (see Table II). This was not observed for the other alkoxide derivatives. The differences in both electronic and ^{1}H NMR spectra must be due to solvent coordination in THF and THF-d_8 solutions; nevertheless, recrystallization of the compound from a THF/n-pentane mixture yielded the unsolvated complex.

$$M[HB(3,5\text{-}Me_2pz)_3]Cl_3(THF) + xNaOR \xrightarrow{THF} M[HB(3,5\text{-}Me_2pz)_3](OR)_xCl_{3-x} + xNaCl \quad (1)$$

(x = 1, M = U; x = 2 and 3, M = U and Th; R = Bu^t, Pr^i and C_6H_2-2,4,6-Me_3).

The failure to obtain the complexes M[HB(3,5-Me_2pz)$_3$](OR)Cl_2 with M = Th and the formation of the more substituted compounds with this element probably reflects some coordinative unsaturation in the monosubstituted case (x = 1) due to the larger Th(IV) ionic radius.

Work-up procedures generally involved extraction and recrystallization to isolate the compounds; the yields obtained were in the range 30–80% with no special attempt being made to optimize the experimental conditions. The compounds are air and moisture sensitive and can be stored at room temperature under nitrogen without noticeable decomposition. The 2,4,6-trimethylphenoxide derivatives are only soluble in ethers and halogenated solvents, whereas all the other compounds are also soluble in aromatic solvents, with the solubility in aliphatic hydrocarbons increasing from the mono- to the tri-substituted complexes.

Proton NMR data are given in Table I. All the uranium complexes exhibit substantial isotropic shifts*, as is typical of uranium(IV) complexes [3]. The spectra of the trisubstituted complexes (**3a**, **3b**, **6a**, **6b**, **9a**, and **9b**) display single signals for the methyl-3 and methyl-5 protons and proton-4 of the pyrazolyl rings, indicating that the three rings are in

*The values in Table I are the shifts relative to TMS; however the isotropic shifts for the uranium complexes can be estimated by comparison with the analogous thorium complexes.

TABLE II. Analytical and Physical Data for Alkoxide and Aryloxide Derivatives of M[HB(3,5-$Me_2pz)_3$]Cl_3(THF)

Complex	Yield (%)	Analysis[a] (%)			IR ν(B–H) (cm^{-1})	Electronic spectrum (nm)
		C	H	N		
U[HB(3,5-$Me_2pz)_3$](OBu^t)Cl_2 (**1**)	75	34.9 (33.6)	4.8 (4.6)	12.0 (12.4)	2550	651m, 671s, 690sh, 973w, 1050m, 1085m, 1198w[b,c]
U[HB(3,5-$Me_2pz)_3$](OBu^t)$_2$Cl (**2a**)	34	38.1 (38.5)	5.2 (5.6)	11.4 (11.7)	2540	637m, 645sh, 681s, 694m, 1115m[b,c]
Th[HB(3,5-$Me_2pz)_3$](OBu^t)$_2$Cl (**2b**)	32	39.4 (38.9)	5.8 (5.7)	11.9 (11.8)	2542	
U[HB(3,5-$Me_2pz)_3$](OBu^t)$_3$ (**3a**)	60	42.3 (42.9)	6.5 (6.5)	10.7 (11.1)	2540	648m, 669m, 700vs, 1133s, 1193s, 1380w[b,c]
Th[HB(3,5-$Me_2pz)_3$](OBu^t)$_3$ (**3b**)	65	44.0 (43.7)	6.7 (6.6)	11.8 (11.2)	2540	
U[HB(3,5-$Me_2pz)_3$](OPr^i)Cl_2 (**4**)	45	33.6 (32.5)	4.6 (4.4)	12.4 (12.6)	2540	671s, 964sh, 1015sh, 1064w, 1124m, 1146s[b]; 650m, 670s, 677m, 971m, 1040m, 1082m[c]
U[HB(3,5-$Me_2pz)_3$](OPr^i)$_2$Cl (**5a**)	60	36.7 (36.6)	5.3 (5.2)	12.4 (12.2)	2540	615w, 626w, 681s, 693m, 1112m[b,c]
Th[HB(3,5-$Me_2pz)_3$](OPr^i)$_2$Cl (**5b**)	51	36.0 (36.9)	5.3 (5.3)	11.6 (12.3)	2537	
[HB(3,5-$Me_2pz)_3$]U(OPr^i)$_3$ (**6a**)	60	40.1 (40.5)	6.2 (6.0)	12.1 (11.8)	2525	648w, 698s, 1126s, 1193m[b,c]
Th[HB(3,5-$Me_2pz)_3$](OPr^i)$_3$ (**6b**)	50	39.5 (40.8)	6.0 (6.1)	11.8 (11.9)	2522	
U[HB(3,5-$Me_2pz)_3$](OC_6H_2-2,4,6-Me_3)Cl_2 (**7**)	78	39.3 (38.9)	4.6 (4.5)	11.4 (11.3)	2545	640m, 661m, 671s, 702w, 942w, 975w, 1027w, 1071m, 1088m, 1121m, 1148sh, 1161sh, 1221w, 1336m[b,c]
U[HB(3,5-$Me_2pz)_3$](OC_6H_2-2,4,6-Me_3)$_2$Cl (**8a**)	70	47.9 (47.1)	5.5 (5.2)	10.3 (10.0)	2540	639m, 667m, 678s, 702m, 1128s[b,c]
Th[HB(3,5-$Me_2pz)_3$](OC_6H_2-2,4,6-Me_3)$_2$Cl (**8b**)	78	47.5 (47.5)	5.5 (5.3)	9.9 (10.1)	2540	
U[HB(3,5-$Me_2pz)_3$](OC_6H_2-2,4,6-Me_3)$_3$ (**9a**)	75	51.6 (53.6)	5.6 (5.8)	8.2 (8.9)	2534	645m, 665m, 682m, 703m, 1127s, 1190m[b,c]
Th[HB(3,5-$Me_2pz)_3$](OC_6H_2-2,4,6-Me_3)$_3$ (**9b**)	76	53.6 (54.0)	6.1 (5.9)	8.5 (9.0)	2530	

[a]Required values in parentheses. [b]In THF. [c]In dichloromethane.

magnetically equivalent environments, as previously observed for the compounds M[HB(3,5-$Me_2pz)_3$]-Cl_3(THF) [1] and M[HB(3,5-$Me_2pz)_3$]($NPh_2)_3$ [2].

The resonances assigned to the polypyrazolylborate ligands in the spectra of compounds **1**, **4** and **7** indicate that only two of the three pyrazolyl rings are equivalent; this 2:1 pattern has already been found for the complexes M[HB(3,5-$Me_2pz)_3$](Cp)-Cl_2 and M[HB(3,5-$Me_2pz)_3$][$N(SiMe_3)_2$]Cl_2 [2] where two 3,5-Me_2pz rings are *trans* to the Cl ligands and the other ring is *trans* to the remaining ligand. For the disubstituted compounds **2a**, **2b**, **5a**, **5b**, **8a** and **8b** the ^{1}H NMR spectra again show non-equivalence of one of the three pyrazolyl rings, which in this case should be the one that is *trans* to the Cl ligand.

In the case of complex **5a**, owing to the prochirality of the uranium centre and of the secondary carbons of the isopropyl fragments, the methyl groups are diastereotopic. Incidentally, at room temperature the two expected resonances are barely seen because they overlap with the resonance due to the H(4) protons of two pyrazolyl rings, so preventing the observation of an unambiguous splitting. Upon lowering the temperature a few degrees, three resonances can be easily distinguished, owing to the different temperature dependence of their chemical shifts.

^{1}H NMR Spectroscopy: Dynamic Studies

Some additional information on the uranium compounds described above can be derived from variable temperature NMR studies*.

The absorption resonance for the *o*-CH_3 protons of the aryl ring in compound **7** is already very broad

*In all studies, spectral changes were found to be independent of concentration and were completely reversible.

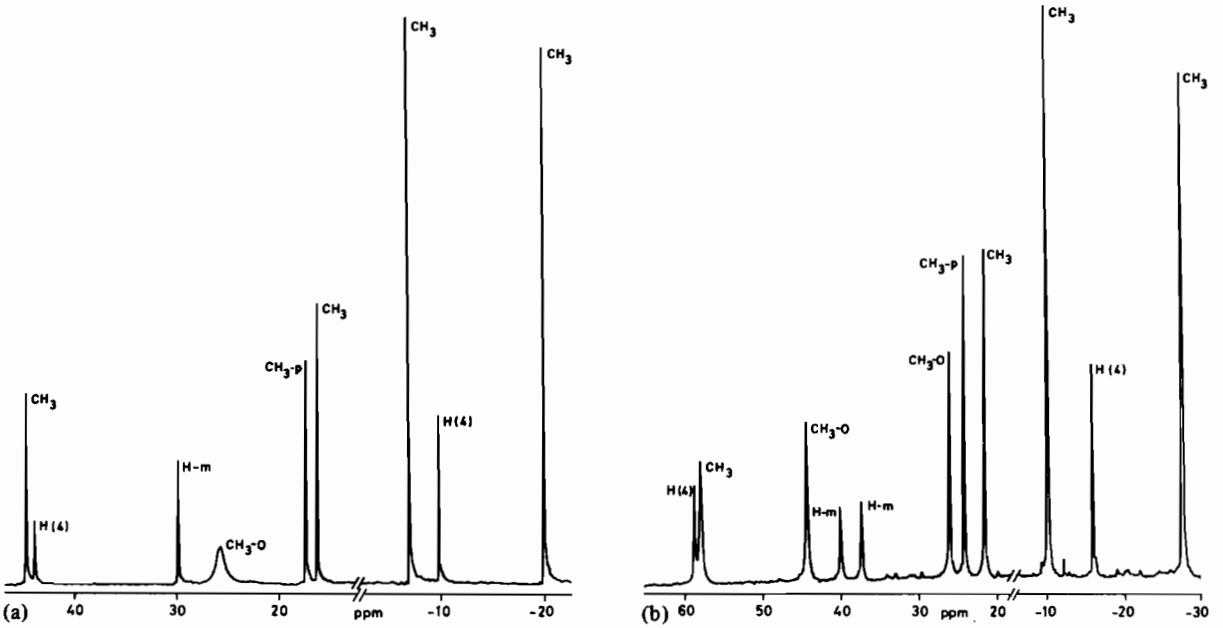

Fig. 1. ^{1}H NMR spectra of U[HB(3,5-Me_2pz)$_3$](OC_6H_2-2,4,6-Me_3)Cl_2 (**10**) in chloroform-d_1: (a) T = 300 K; (b) T = 210 K.

at room temperature (Fig. 1a). Upon lowering the temperature the absorption collapses and gives rise to two signals in a 1:1 intensity ratio (Fig. 1b). The same behaviour is observed for the *m*-H of the aryl ring. This is indicative of hindered rotation of the aryloxide group. The free energy of activation for the rotation can be estimated from $\Delta\nu$ at the coalescence temperature (T_c = 277 K) [4]. As the temperature dependence of the chemical shifts of the protons of the *o*-CH_3 groups was found to obey an approximate Curie relationship below the coalescence temperature ($\delta_1 = 7.17 \times 10^3\ T^{-1} + 11.23$; $\delta_2 = 4.91 \times 10^3\ T^{-1} + 3.44$), extrapolation of these data yields $\Delta\nu$ = 1275 Hz and $\Delta G^{\ddagger}$ = 49 ± 4 kJ mol^{-1}. The same $\Delta G^{\ddagger}$ value was obtained using the absorption resonances for the *m*-H protons of the aryl ring ($\delta_1 = 4.69 \times 10^3\ T^{-1} + 15.50$; $\delta_2 = 5.71 \times 10^3\ T^{-1} + 13.65$; $\Delta\nu$ = 170 Hz at T_c = 253 K). Hindered rotation of aryloxide groups has also been observed in the compound U(HBpz_3)$_2$(OC_6H_2-2,4,6-Me_3)Cl ($\Delta G^{\ddagger}$ = 62 ± 5 kJ mol^{-1}) [5].

The free energy for rotation of the aryloxide groups in compound **8a** was also estimated. However, in this case as the coalescence temperature of the absorption resonance for the *o*-CH_3 protons of the aryl ring is 225 K there was only a short temperature range available to calculate δ *versus* T^{-1} because the melting point of the solvent (deuterated chloroform) is just below 210 K. An approximate method was therefore used and $\Delta\nu$ was evaluated as the width at half maximum intensity of the exchange broadened signal (W') at T_c. This bandwidth was calculated by extrapolation in a plot of $\ln(W' - W_o)$ *versus* T^{-1}, where W_o is the width in the absence of exchange [4]. The value obtained for $\Delta G^{\ddagger}$ was 41 ± 3 kJ mol^{-1}. The same value was obtained applying an identical treatment to the absorption resonances of the *m*-H protons which coalesce at about 210 K.

While these spectral changes occur for the aryloxide derivatives, the absorption resonances of the pyrazolyl ring protons display an interesting feature; upon lowering the temperature these signals broaden and then become narrow again. This effect is more evident in the case of complex **7**, especially for the protons of CH_3(3) of the pyrazolyl ring which is *trans* to the OR ligand. The dependence of the chemical shifts with temperature shows Curie–Weiss behaviour with different slopes above and below the temperature range where maximum broadening occurs. This is indicative of an exchange process and must be related to a change from a conformation where the OR ligand is freely rotating to a lower energy conformer, at low temperature, when the OR group rotation is hindered. Actually, $\Delta G^{\ddagger}$ for this process, estimated from the bandwidth of the CH_3(3) resonance at 260 K (maximum bandwidth), yields 51 ± 4 kJ mol^{-1}, a value which compares favourably with the value of $\Delta G^{\ddagger}$ estimated above for the barrier to rotation of the aryloxide group in complex **7**.

Line broadening and narrowing of the resonances of the protons of the pyrazolyl rings is also observed for the isopropoxide and t-butoxide derivatives, as well as for the resonances of the protons of the R groups of the alkoxide ligands in these compounds. This must also be related to restricted rotation of the OR groups. In the case of the monoisopropoxide derivative **4** the absence of splitting of the methyl

resonances at low temperature could be explained by the occurrence of two lower energy conformers of the type

However, as the absence of splitting is also observed for the diisopropoxide derivative **5a** as well as for the mono- and di-t-butoxide derivatives **1** and **2a**, free rotation around the O–R bond can be assumed. So, the spectral changes observed for these compounds upon lowering the temperature can be explained if restricted rotation around the U–O bond is assumed.

For the aryloxide derivatives discussed above, the *ortho* methyl substituents of the aryl ring cause additional steric effects that hinder the rotation about the O–R bond.

The observed change of conformation in the above complexes can be explained if a U–O–C angle smaller than 180° is assumed. In fact, if the U–O–C angle were 180° no difference could be envisaged between the conformation where the OR ligand is freely rotating and a lower energy conformer. It has been observed before that these angles are indeed strongly dependent on steric effects and in less congested complexes they are substantially less than 180° [6, 7]. For uranium compounds containing aryloxides, U–O–C angles of 158 and 165° were found for $Cp''_2U(OAr)_2$ [6] and U–O–C angles of 149.4, 150.4, and 163.4° were found for $U(NEt_2)(OAr'')_3$ [8]. It is also interesting to note two molybdenum complexes containing polypyrazolylborate and alkoxide ligands; in $Mo[HB(3,5\text{-}Me_2\text{-}4\text{-}Clpz)_3](OPr^i)Cl(NO)$ the M–O–C angle is 132.4° [9] and in $Mo[HB(3,5\text{-}Me_2pz)_3](OPr^i)_2(NO)$ it is 133.4° [10].

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