

Uranium complexes with hydrotris(pyrazolyl) borate

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Abstract

Uranium tetraiodide, prepared by a high temperature method, reacts with two equivalents of KHBpz_3 in CH_2Cl_2 giving the orange compound $[\text{UI}_2(\text{HBpz}_3)_2]$ (1) in 62% yield. The same reaction in THF provides the compound $[\text{UI}(\text{O}(\text{CH}_2)_4\text{I})(\text{HBpz}_3)_2]$ (2) in 66% isolated yield and arising from ring opening of THF by the uranium tetraiodide. The solid state structure of compound 2 has been determined by X-ray crystallography. Compound 1 reacts with NaOC_2H_5 in the molar ratio 1:1 giving the monoalkoxide $[\text{UI}(\text{OC}_2\text{H}_5)(\text{HBpz}_3)_2]$ (3), which crystallizes in the monoclinic space group $P2_1/n$. X-ray crystallographic analysis shows that in complexes 2 and 3 the uranium is 8-coordinate with the two tridentate HBpz_3 ligands, iodide, and alkoxide displaying square antiprismatic geometry. The solid state structure of the analogous monomeric compound $[\text{UCl}(\text{OC}_2\text{H}_5)(\text{HBpz}_3)_2]$ (4) is also described and compared with those of compounds 2 and 3.

Keywords: Uranium; Iodides; Chloride; X-ray diffraction; Nuclear magnetic resonance; Pyrazole

1. Introduction

Most of the chemistry that has been done with U(IV) involves the use of UCl_4 as starting material. This halide has been successfully used to synthesize complexes of the type $[\text{UCl}_2\text{L}_2]$ ($\text{L} = \text{HBpz}_3$, C_5Me_5 , $\text{C}_5\text{H}_3-1,3(\text{SiMe}_3)_2$, $\text{C}_6\text{H}_5\text{Co}[\text{P}(\text{O})(\text{OEt})_2]_3$, $\text{C}_4\text{Me}_4\text{P}$) in tetrahydrofuran [1–5]. However iodide derivatives of this type are rare and those described have been obtained by reaction of $[\text{UR}_2(\text{C}_5\text{Me}_5)_2]$ ($\text{R} = \text{alkyl}$) with I_2 , or of $[\text{UCl}_2\{\text{C}_5\text{H}_3-1,3(\text{SiMe}_3)_2\}_2]$ with BI_3 [6,7]. To our knowledge, Lewis base adducts of uranium tetraiodide of the type $[\text{UI}_4\text{L}_2]$ ($\text{L} = \text{N}, \text{N}, \text{N}', \text{N}'\text{-tetramethylurea}$, $\text{Ph}_3\text{P}=\text{O}$, $\text{Ph}_2\text{C}=\text{O}$, or CH_3CN) [8] or uranium tetraiodide prepared by a high temperature method [9], have rarely been used as precursors for the synthesis of iodo organocompounds of uranium(IV). One of the few examples is $[\text{UI}(\text{C}_9\text{H}_7)_3]$ from UI_4 [10].

As part of our investigation of uranium complexes with polypyrazolylborates we were interested in synthesizing iodo compounds of uranium(III) and(IV) with $\text{HB}(3,5\text{-Me}_2\text{pz})_3$. In previous work we have shown that uranium tetraiodide promotes the ring-opening of tetrahydrofuran, owing to its Lewis acidity, and that the

uranium iodobutoxide formed is a good starting material for the synthesis of the alkoxide $[\text{UI}_2\{\text{O}(\text{CH}_2)_4\text{I}\}\{\text{HB}(3,5\text{Me}_2\text{pz})_3\}]$ [11]. To avoid the formation of the iodobutoxide we used solvents other than THF in reactions of UI_4 with polypyrazolylborates. In this work we report the reaction of UI_4 with two equivalents of KHBpz_3 using dichloromethane or tetrahydrofuran as solvent.

2. Experimental section

2.1. General procedures

All reactions were carried out under argon, using standard Schlenk and vacuum-line techniques, or in an argon-filled glove-box. Solvents were dried and deoxygenated by standard methods [12] and distilled immediately prior use. CDCl_3 was dried over P_2O_5 , and C_6D_6 was dried over $\text{Na}/\text{benzophenone}$. UCl_4 [13], UI_4 [9], KHBpz_3 [14], $[\text{UCl}_2(\text{HBpz}_3)_2]$ [1], and $[\text{UCl}(\text{OC}_2\text{H}_5)(\text{HBpz}_3)_2]$ [15] were prepared by published methods, NaOC_2H_5 was prepared by the reaction of Na with ethanol.

^1H NMR spectra were recorded on a Bruker SY80FT multinuclear spectrometer, using the chemical shift of the solvent as the internal standard. IR spectra

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were recorded as Nujol mulls on a Perkin Elmer 577 spectrophotometer. Absorption electronic spectra were recorded as solutions on a Cary 2390 Varian spectrometer. Carbon, hydrogen and nitrogen analyses were performed on a Perkin Elmer automatic analyser.

2.2. Synthesis and characterization of $[UI_2(HBpz_3)_2]$ (1)

To a suspension of UI_4 (593 mg, 0.79 mmol) in CH_2Cl_2 (40 cm³) was added slowly $KHBpz_3$ (402 mg, 1.59 mmol). The clear dichloromethane became slowly orange and after overnight reaction at room temperature the orange solution formed was separated from the solid by centrifugation. The dichloromethane was evaporated on the vacuum-line and the resulting orange solid was washed with hexane (450 mg, 0.49 mmol, yield 62%).

Anal. Calcd. for $C_{18}H_{20}B_2I_2N_{12}U$: C, 23.6; H, 2.2; N, 18.3. Found: C, 24.1; H, 2.3; N, 17.9%. IR, ν (cm⁻¹): 2480(m) ν (B–H), 1500(s), 1450(s), 1400(s), 1380(m), 1290(s), 1255(w), 1210(s), 1190(m), 1170(w), 1120(s), 1060(m), 1040(s), 970(s), 910(w), 885(w), 860(w), 800(m), 770(s), 720(s), 660(m), 610(m), 330(m). UV-vis. (CH_2Cl_2 , THF or toluene) (λ_{max} , nm): 670(m), 690(s), 1090(s), 1190(s), 1240(vw), 1480(m).

2.3. Synthesis and characterization of $[UI\{O(CH_2)_4I\}(HBpz_3)_2]$ (2)

20 cm³ of THF were added to 264 mg (0.35 mmol) of UI_4 giving a bright red solution, that turned bright

green after 1 h. To this green solution were added 178 mg (0.7 mmol) of $KHBpz_3$. After being stirred for 6 h at room temperature the suspension was centrifuged and the green supernatant was evaporated under vacuum giving a green solid. This solid was recrystallized from toluene/hexane yielding, after drying, 230 mg of product (0.23 mmol, yield 66%).

Anal. Calcd. for $C_{22}H_{28}B_2I_2N_{12}OU$: C, 26.67; H, 2.85; N, 16.98. Found: C, 26.52; H, 3.01; N, 16.70%. IR ν (cm⁻¹): 2450(s) ν (B–H), 1495(s), 1460(w), 1395(s), 1375(m), 1290(s), 1260(s), 1210(s), 1190(m), 1160(w), 1120(w), 1080(w), 1070(w), 980(s), 910(m), 860(m), 800(s), 770(s), 690(m), 610(m), 580(m), 530(m), 500(w), 470(m), 330(m), 280(w). UV-vis. (THF) (λ_{max} , nm): 430(w), 455(s), 510(m), 540(w), 600(m), 660(m), 730(m), 950(s), 1020(s), 1045(s), 1100(w), 1120(w), 1250(s), 1390(s), 1470(s).

2.4. Synthesis and characterization of $[UI(OC_2H_5)(HBpz_3)_2]$ (3)

To a suspension of $[UI_2(HBpz_3)_2]$ (140 mg, 0.15 mmol) in toluene (10 cm³) was added $NaOC_2H_5$ (11 mg, 0.15 mmol). The orange solution of the diiodide turned green almost immediately after addition of the alkoxide. After overnight reaction, the bright green solution was separated by centrifugation and evaporated to dryness, yielding a green crystalline solid (66 mg, yield 52%).

Anal. Calcd. for $C_{20}H_{25}B_2IN_{12}OU$: C, 28.73; H, 3.01; N, 20.10. Found: C, 28.56; H, 2.95; N, 19.80%. IR

Table 1
Crystallographic data for 2, 3 and 4

Compound	$[UI\{O(CH_2)_4I\}(HBpz_3)_2]$ (2)	$[UI(OC_2H_5)(HBpz_3)_2]$ (3)	$[UCl(OC_2H_5)(HBpz_3)_2]$ (4)
Formula	$C_{22}H_{28}B_2I_2N_{12}OU \cdot C_4H_8O$	$C_{20}H_{25}B_2IN_{12}OU$	$C_{20}H_{25}B_2ClN_{12}OU$
Molecular weight	1062.1	835.6	744.6
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	<i>Pbca</i>	<i>P2₁/n</i>	<i>Pbca</i>
<i>a</i> (Å)	15.572(2)	11.581(3)	14.821(1)
<i>b</i> (Å)	18.066(3)	22.493(2)	18.344(2)
<i>c</i> (Å)	26.254(3)	12.272(4)	20.162(3)
α (°)	90	90	90
β (°)	90	101.95(2)	90
γ (°)	90	90	90
<i>V</i> (Å ³)	7386	3128	5482
<i>Z</i>	8	4	8
<i>D</i> _{calc} (g cm ⁻³)	1.910	1.775	1.804
μ (Mo-K α)(cm ⁻¹)	57.9	59.1	57.8
2 θ range (°)	3.0–54.0	3.0–48.0	3.0–50.0
Number of reflections ($F_o > 3\sigma(F_o)$)	3653	3633	2580
Decay corrections, min, max	1.00001, 1.01473	1.00000, 1.00301	1.00001, 1.00811
Range in abs. correction factors	0.7352–1.0000	0.7786–0.9970	0.6943–0.9996
Number of parameters refined	383	338	344
Weighting scheme used, $W = (\sigma^2(F_o) + gF_o^2)^{-1}$, g	0.0005	0.0003	0.00007
Final <i>R</i> , <i>R</i> _w	0.082, 0.069	0.050, 0.051	0.041, 0.031

$\nu(\text{cm}^{-1})$: 2450(s) $\nu(\text{B-H})$, 1500(s), 1450(s), 1400(s), 1375(s), 1295(s), 1255(m), 1210(s), 1190(s), 1125(s), 1115(s), 1100(m), 1060(m), 970(m), 920(w), 915(m), 890(m), 800(w), 770(s), 730(m), 690(w), 655(m), 615(m), 540(w), 515(w), 470(w), 380(w), 330(m). UV-vis. (THF) ($\lambda_{\text{max}}(\text{nm})$): 420(w), 435(w), 450(s), 505(m), 540(m), 595(s), 630(s), 730(m), 840(w), 950(m), 1020(s), 1040(s), 1100(vw), 1120(w), 1240(s), 1390(s), 1470(s).

2.5. Crystallographic analyses

Crystals of **2**, **3** and **4**, obtained by slow diffusion of n-hexane into saturated solutions of the compounds **2** and **3** in toluene and of **4** in THF, were mounted in glass capillaries in an argon-filled glove-box and sealed under argon. Data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromatized Mo-K α radiation, using a ω -2 θ scan mode. Unit cell dimensions were obtained by least-squares refinement of the setting angles of 25 reflections with $14 < 2\theta < 32^\circ$. A summary of the crystal data, data collection and refinement is given in Table 1. Data were corrected for Lorentz-polarization effects, for linear decay and for absorption by empirical corrections based on ψ scans, using the ENRAF-NONIUS program. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares [16].

The structural analysis of **2** revealed one THF solvent molecule with large thermal parameters and much disorder.

The structural analysis of **3** showed large thermal parameters for the ethoxide carbon atoms (C(1) and C(2)), giving chemically unsatisfactory bond distances in the refinements. The difference Fourier map showed additional electron density in the region of the C(1) and C(2) atoms, indicating disorder. Attempts to find a model for the disorder was unsuccessful, and so restraints on the interatomic distances of the disordered atoms were applied (the distance restraints applied were: O–C(1), $1.42 \pm 0.02 \text{ \AA}$; C(1)–C(2), $1.37 \pm 0.02 \text{ \AA}$). In the residual electron density map a set of three peaks were located (C(3), C(4) and C(5)) which were assumed to be a disordered solvent molecule, but to which no chemical identity could be assigned. They were introduced into the refinement as full-occupancy carbon atoms. The lattice solvent was then excluded from the formula, from the molecular weight and from the calculation of the density in Table 1.

For **2** all the non-hydrogen atoms were refined anisotropically except the THF atoms. For **3** all the non-hydrogen atoms were refined anisotropically except the disordered C(1) and C(2) atoms and the solvent atoms, and in **4** all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions, constrained to ride on

Table 2
Fractional atomic coordinates for [UI(O(CH₂)₄)I(HBpz₃)₂]

Atom	x	y	z
U	0.15581(5)	0.25559(4)	0.14561(3)
I(1)	0.2035(1)	0.1829(1)	0.0411(1)
I(2)	0.5691(2)	0.1345(1)	0.0726(1)
O(1)	0.2784(8)	0.2906(7)	0.1489(5)
N(1)	0.0382(10)	0.1898(9)	0.2017(7)
N(2)	0.1991(11)	0.2623(9)	0.2410(7)
N(3)	0.2158(10)	0.1280(9)	0.1745(7)
N(4)	0.0153(12)	0.2581(11)	0.0945(7)
N(5)	0.1585(14)	0.3691(9)	0.0889(7)
N(6)	0.0592(11)	0.3573(8)	0.1833(7)
N(11)	0.0532(12)	0.1500(9)	0.2439(7)
N(21)	0.1891(10)	0.2095(9)	0.2769(7)
N(31)	0.1992(11)	0.0963(9)	0.2211(7)
N(41)	-0.0292(12)	0.3206(9)	0.0809(7)
N(51)	0.0891(13)	0.4152(11)	0.0788(7)
N(61)	0.0039(10)	0.4014(9)	0.1571(6)
C(1)	0.3679(12)	0.3068(13)	0.1547(10)
C(2)	0.4191(13)	0.2665(14)	0.1163(10)
C(3)	0.5140(13)	0.2819(13)	0.1225(10)
C(4)	0.5673(18)	0.2530(15)	0.0783(10)
C(11)	-0.0176(13)	0.1369(12)	0.2683(9)
C(12)	-0.0845(12)	0.1677(12)	0.2422(10)
C(13)	-0.0454(14)	0.1986(11)	0.2018(9)
C(21)	0.2229(14)	0.2299(11)	0.3199(8)
C(22)	0.2590(14)	0.2983(14)	0.3158(10)
C(23)	0.2423(15)	0.3170(12)	0.2633(10)
C(31)	0.2429(14)	0.0306(11)	0.2252(10)
C(32)	0.2890(15)	0.0202(13)	0.1795(11)
C(33)	0.2680(13)	0.0810(13)	0.1525(9)
C(41)	-0.0993(15)	0.3029(14)	0.0530(10)
C(42)	-0.1023(18)	0.2268(14)	0.0476(10)
C(43)	-0.0284(19)	0.2027(14)	0.0745(11)
C(51)	0.1165(22)	0.4707(13)	0.0471(10)
C(52)	0.2045(21)	0.4631(14)	0.0425(12)
C(53)	0.2292(16)	0.3985(13)	0.0667(10)
C(61)	-0.0473(15)	0.4397(13)	0.1869(10)
C(62)	-0.0238(18)	0.4236(13)	0.2347(12)
C(63)	0.0427(15)	0.3722(12)	0.2333(11)
B(1)	0.1464(17)	0.1374(14)	0.2627(10)
B(2)	0.0027(20)	0.3968(14)	0.0970(11)
O(2)	0.4498(18)	0.4949(15)	0.1044(11)
C(5)	0.4880(23)	0.4571(19)	0.0577(14)
C(6)	0.5887(19)	0.4573(16)	0.0642(12)
C(7)	0.6229(25)	0.4897(21)	0.1118(16)
C(8)	0.5320(21)	0.5159(16)	0.1397(13)

their carbon and boron atoms with group U_{ISO} values assigned. The hydrogen atoms on the disordered atoms and the solvent molecules were not included.

In the final difference Fourier the two largest electron density peaks were 2.0 and 1.9 e \AA^{-3} for compound **2** and were near the disordered THF molecule; for **3** the two highest peaks were 1.3 and 1.1 e \AA^{-3} , near the disordered C(1) and C(2) atoms; for **4** the two highest peaks were $\sim 1 \text{ e \AA}^{-3}$ and were near the U atom.

Final atomic coordinates for **2**, **3** and **4** are listed in Tables 2–4.

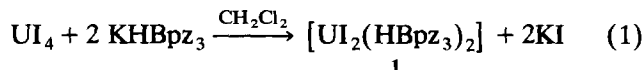
Atomic scattering factors and anomalous dispersion terms were taken from the *International Tables for X-ray Crystallography*.

Complete bond distances, angles, anisotropic thermal parameters, hydrogen atom coordinates, and least-squares planes have been deposited with the Cambridge Crystallographic Data Center, and these together with structure factor tables are provided in supplementary material (available from the authors).

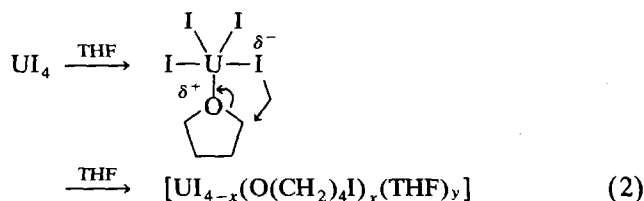
3. Results and discussion

Uranium tetraiodide reacts with two equivalents of potassium hydrotris(pyrazolyl)borate in dichloromethane

to yield microcrystalline orange $[\text{UI}_2(\text{HBpz}_3)_2]$ (**1**) in ca 65% isolated yield (Eq. (1)):

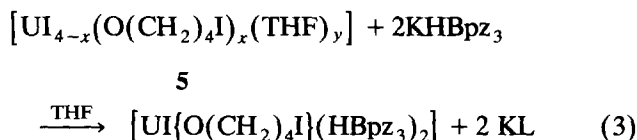


However, when the same reaction is run in THF the monoalkoxide $[\text{UI}(\text{O}(\text{CH}_2)_4\text{I})(\text{HBpz}_3)_2]$ (**2**) is isolated in 66% yield. In a previous work we have shown that UI_4 promotes the opening of THF due to its Lewis acidity, leading to the formation of a uranium iodobutoxide that we formulated as **5** [11]. This species reacts with two equivalents of KHBpz_3 giving compound **2** with a reasonable yield (Eqs. (2) and (3)):



5

$x = 1 \text{ or } 2; y \neq 1$



2

$x = 1, L = \text{I}$

or

$x = 2, L = \text{I} \text{ and } [\text{O}(\text{CH}_2)_4\text{I}]$

The possibility of using compound **1** for the synthesis of iodo compounds of U(IV) of the same type as **2** was evaluated with the reaction of one equivalent of sodium ethoxide with compound **1** in toluene. After workup the monoalkoxide $[\text{UI}(\text{OC}_2\text{H}_5)(\text{HBpz}_3)_2]$ (**3**) was isolated in 52% yield. This compound can also be prepared by reaction of **1** with an excess of ethanol. We observed that, independent of the stoichiometry used, compound **1** reacts with ethanol or phenol to yield only monosubstituted alkoxides (the compound $[\text{UI}(\text{OC}_6\text{H}_5)(\text{HBpz}_3)_2]$ was only identified by ^1H NMR spectroscopy: see Table 5).

The orange compound **1** is soluble in CH_2Cl_2 and THF and slightly soluble in toluene and benzene. Compounds **2** and **3** are very soluble in THF, toluene, and benzene, and slightly soluble in aliphatic hydrocarbons.

The IR spectra of the hydrotris(pyrazolyl)borato complexes **1–3** show the bands characteristic of polypyrazolylborate $\nu(\text{B-H})$ at 2480 cm^{-1} for **1** and at 2450 cm^{-1} for **2** and **3**. The decrease in frequency of $\nu(\text{B-H})$, when one iodide is replaced by one alkoxide is similar to what has been observed for other similar compounds of uranium [1,15].

Table 3

Fractional atomic coordinates for $[\text{UI}(\text{OC}_2\text{H}_5)(\text{HBpz}_3)_2]$

Atom	x	y	z
U	0.35498(4)	0.67388(2)	0.16564(4)
I	0.62462(8)	0.65064(5)	0.1801(1)
O	0.3622(8)	0.7223(4)	0.0279(6)
N(1)	0.2957(9)	0.6719(5)	0.3618(8)
N(2)	0.2039(9)	0.7556(4)	0.1606(8)
N(3)	0.4511(8)	0.7648(4)	0.2776(8)
N(4)	0.1512(8)	0.6231(4)	0.1448(8)
N(5)	0.3948(10)	0.5673(4)	0.2502(8)
N(6)	0.3307(9)	0.5979(5)	0.0096(8)
N(11)	0.2735(9)	0.7217(5)	0.4133(8)
N(21)	0.1826(9)	0.7866(4)	0.2495(9)
N(31)	0.3967(9)	0.7989(4)	0.3422(8)
N(41)	0.1311(9)	0.5635(5)	0.1254(9)
N(51)	0.3237(10)	0.5195(5)	0.2144(10)
N(61)	0.2837(9)	0.5417(5)	0.0103(9)
C(1)	0.3784(28)	0.7512(14)	-0.0779(19)
C(2)	0.4019(33)	0.8062(16)	-0.0448(29)
C(3)	0.5641(34)	-0.0031(16)	1.0860(27)
C(4)	0.5448(33)	0.0321(15)	0.9212(28)
C(5)	0.6612(30)	0.0337(16)	1.0289(30)
C(11)	0.2322(13)	0.7084(7)	0.5055(12)
C(12)	0.2272(14)	0.6472(8)	0.5149(13)
C(13)	0.2664(12)	0.6273(6)	0.4244(11)
C(21)	0.0885(13)	0.8216(7)	0.2176(16)
C(22)	0.0455(14)	0.8129(6)	0.1073(18)
C(23)	0.1202(12)	0.7710(6)	0.0721(13)
C(31)	0.4596(13)	0.8492(6)	0.3771(11)
C(32)	0.5592(13)	0.8475(6)	0.3325(11)
C(33)	0.5506(12)	0.7942(6)	0.2717(11)
C(41)	0.0220(12)	0.5493(6)	0.1327(11)
C(42)	-0.0309(12)	0.5996(7)	0.1670(11)
C(43)	0.0528(11)	0.6439(7)	0.1731(10)
C(51)	0.3630(17)	0.4720(6)	0.2771(14)
C(52)	0.4587(16)	0.4884(8)	0.3563(14)
C(53)	0.4765(12)	0.5494(7)	0.3370(11)
C(61)	0.3049(13)	0.5102(8)	-0.0762(14)
C(62)	0.3650(16)	0.5427(10)	-0.1304(15)
C(63)	0.3809(13)	0.5996(8)	-0.0765(12)
B(1)	0.2701(15)	0.7845(7)	0.3615(14)
B(2)	0.2301(15)	0.5205(7)	0.1072(14)

For compound **1** the electronic absorption spectrum in THF solution shows absorption bands with positions and relative intensities consistent with Laporte-forbidden $f \rightarrow f$ transitions of the uranium (IV) center. The pattern of the spectrum is maintained when the solvent is CH_2Cl_2 and is very similar to that of the analogous compound $[\text{UCl}_2(\text{HBpz}_3)_2]$ in the same solvents. For compounds **2** and **3** the electronic absorption spectra present also the same pattern when the solvents are THF or CH_2Cl_2 , but the substitution of one iodide by one alkoxide changes the splitting and the relative intensities of the absorption bands (see experimental details).

3.1. Crystal structure of $[\text{UI}\{\text{O}(\text{CH}_2)_4\text{I}\}(\text{HBpz}_3)_2]$ (**2**)

The crystal structure of **2** consists of monomeric molecules in which the uranium atom is eight-coordinate and displays approximately square antiprismatic (SAP) geometry. One "square" face of the polyhedron

N(1) N(3) I(1) N(4) is distorted from planarity (the dihedral angle δ for one of the diagonals is 7.3°), while the face N(2) O(1) N(5) N(6) is approximately planar (root-mean-square deviation of 0.0383 \AA ; $\delta = 3.9^\circ$). Consequently the coordination polyhedron can be considered on the geometric pathway from SAP to bicapped trigonal prism (BCTP). A PLUTO drawing of **2** is shown in Fig. 1; selected bond lengths and angles are listed in Table 6.

The U–N bond distances range from $2.54(2)$ to $2.63(2) \text{ \AA}$, with a mean value of $2.58(3) \text{ \AA}$, which can be compared with the corresponding average values of $2.55(2) \text{ \AA}$, $2.60(3) \text{ \AA}$ and $2.57(2) \text{ \AA}$ found in the eight-coordinate complexes $[\text{UCl}_2(\text{HBpz}_3)_2]$, $[\text{UCl}(\text{O}^t\text{Bu})(\text{HBpz}_3)_2]$ and $[\text{UCl}(\text{OC}_6\text{H}_5)(\text{HBpz}_3)_2]$ [**1c**,**15**]. The U–I(1) bond distance of $3.131(5) \text{ \AA}$ is longer than the corresponding distance observed in $[\text{UI}_2\{\text{C}_5\text{H}_3-1,3(\text{SiMe}_3)_2\}_2]$ ($2.953(2) \text{ \AA}$) [7], probably owing to the larger size and different shape of the $(\text{HBpz}_3)^-$ compared to $\text{C}_5\text{H}_3-1,3(\text{SiMe}_3)_2^-$. Based on a cone angle

Table 4
Fractional atomic coordinates for $[\text{UCl}(\text{OC}_2\text{H}_5)(\text{HBpz}_3)_2]$

Atom	x	y	z
U	0.33517(2)	0.05441(2)	0.31421(2)
Cl	0.4374(2)	-0.0658(1)	0.3282(2)
O	0.2433(5)	-0.0083(3)	0.2662(4)
N(1)	0.2679(6)	0.1357(5)	0.2212(5)
N(2)	0.4195(5)	0.1812(4)	0.3128(6)
N(3)	0.4399(5)	0.0538(5)	0.2129(4)
N(4)	0.4187(6)	0.0757(4)	0.4234(5)
N(5)	0.2531(6)	-0.0084(4)	0.4108(5)
N(6)	0.2375(6)	0.1492(4)	0.3780(5)
N(11)	0.3151(6)	0.1808(4)	0.1803(5)
N(21)	0.4419(6)	0.2168(4)	0.2551(6)
N(31)	0.4593(6)	0.1134(5)	0.1735(6)
N(41)	0.3796(7)	0.0964(5)	0.4818(5)
N(51)	0.2420(7)	0.0184(5)	0.4726(5)
N(61)	0.2309(6)	0.1519(5)	0.4445(5)
C(1)	0.1900(9)	-0.0563(8)	0.2265(8)
C(2)	0.2319(12)	-0.1188(8)	0.2044(9)
C(11)	0.2605(9)	0.2082(6)	0.1336(6)
C(12)	0.1766(9)	0.1822(6)	0.1441(7)
C(13)	0.1834(7)	0.1361(6)	0.1988(7)
C(21)	0.4742(8)	0.2834(6)	0.2709(7)
C(22)	0.4704(9)	0.2911(6)	0.3383(7)
C(23)	0.4377(8)	0.2271(6)	0.3628(6)
C(31)	0.5045(9)	0.0913(8)	0.1194(7)
C(32)	0.5188(8)	0.0171(8)	0.1221(7)
C(33)	0.4752(8)	-0.0034(6)	0.1802(7)
C(41)	0.4430(8)	0.1078(6)	0.5262(6)
C(42)	0.5260(8)	0.0976(6)	0.4992(7)
C(43)	0.5069(7)	0.0750(5)	0.4347(6)
C(51)	0.2050(8)	-0.0306(7)	0.5133(7)
C(52)	0.1906(9)	-0.0936(7)	0.4756(7)
C(53)	0.2235(8)	-0.0764(6)	0.4122(7)
C(61)	0.1842(8)	0.2119(6)	0.4619(7)
C(62)	0.1602(9)	0.2486(6)	0.4056(7)
C(63)	0.1952(7)	0.2088(5)	0.3550(7)
B(1)	0.4199(8)	0.1888(7)	0.1859(10)
B(2)	0.2750(10)	0.0950(8)	0.4900(7)

Table 5
 ^1H NMR data at room temperature ^a

COMPLEX	HBpz ₃				Other resonances	Ref.
	H(3)	H(4)	H(5)	(B-H)		
[U ₂ (HBpz ₃) ₂] (1)	14.7 (6H, s)	7.1 (6H, s)	6.3 (6H, s)	–	–	This work
[U{O(CH ₂) ₄ I}(HBpz ₃) ₂] (2)	32.6 (6H, s)	6.9 (6H, s)	– 1.2 (6H, s)	– 20.1 (2H, m)	206.9(2H, lw = 20Hz, CH ₂) 80.9(2H, lw = 20Hz, CH ₂) 46.1(2H, lw = 20Hz, CH ₂) 22.1(2H, t, J = 8Hz, CH ₂)	This work
[U(OC ₂ H ₅)(HBpz ₃) ₂] (3)	33.9 (6H, s)	6.8 (6H, s)	– 1.3 (6H, s)	– 20.8 (2H, m)	209.2(2H, lw = 19Hz, CH ₂) 79.1(3H, lw = 16Hz, CH ₃)	This work
[UCl(OC ₂ H ₅)(HBpz ₃) ₂] (4)	31.2 (6H, s)	6.5 (6H, s)	– 0.9 (6H, s)	– 18.9 (2H, m)	187.5(2H, lw = 15Hz, CH ₂) 71.1(3H, lw = 15Hz, CH ₃)	[15]
[U(OC ₆ H ₅)(HBpz ₃) ₂] (6)	34.2 (6H, s)	7.5 (6H, s)	– 0.7 (6H, s)	– 19.7 (2H, m)	80.4(2H, lw = 27Hz, o-H) 41.4(2H, t, J = 8Hz, m-H) 29.3(1H, t, J = 8Hz, p-H)	This work
[UCl(OC ₆ H ₅)(HBpz ₃) ₂] (6)	30.9 (6H, s)	6.6 (6H, s)	– 0.5 (6H, s)	– 17.9 (2H, m)	70.0(2H, d, J = 7Hz, o-H) 35.8(2H, t, J = 7Hz, m-H) 25.9(1H, t, J = 7Hz, p-H)	[15]
[UCl ₂ (HBpz ₃) ₂] ^b	21.6 (6H, s)	7.5 (6H, s)	3.6 (6H, s)	– 10.9 (2H, m)	–	[1(b)]
[ThCl ₂ (HBpz ₃) ₂] ^c	7.5 (6H, dd)	6.1 (6H, t)	7.7 (6H, d)	4.6 (2H, m)	–	[1(c)]

^a The chemical shifts are in ppm from TMS; downfield shifts are positive; s = singlet, t = triplet; d = doublet, dd = doublet of doublets, m = multiplet; all the spectra were run in benzene-*d*₆; except ^b in CH₂Cl₂-*d*₂ and ^c in CHCl₃-*d*₁.

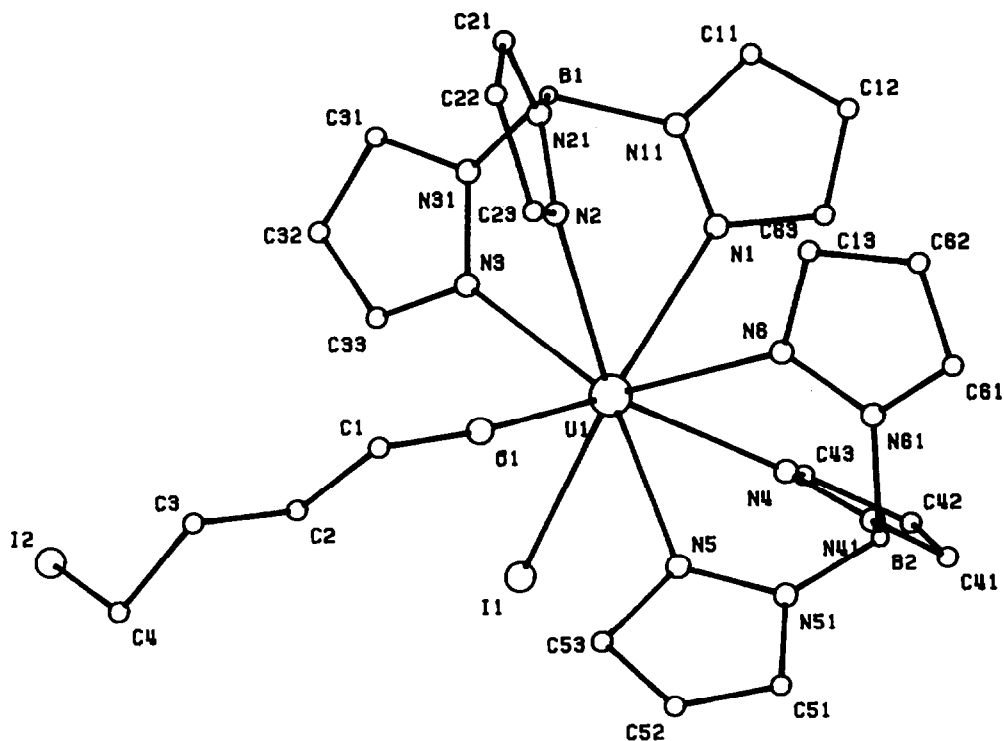


Fig. 1. PLUTO view of [U{O(CH₂)₄I}(HBpz₃)₂].

Table 6
Selected bond lengths (Å) and bond angles (°) for [U(O(CH₂)₄I)-(HBpz₃)₂]

U–I(1)	3.131(5)	O(1)–C(1)	1.43(2)
U–O(1)	2.012(14)	C(1)–C(2)	1.48(3)
U–N(1)	2.63(2)	C(2)–C(3)	1.51(3)
U–N(2)	2.60(2)	C(3)–C(4)	1.52(3)
U–N(3)	2.60(2)	C(4)–I(2)	2.15(3)
U–N(4)	2.57(2)	C–C ^a	1.38(3)
U–N(5)	2.54(2)	C–N ^a	1.33(3)
U–N(6)	2.57(2)	N–N ^a	1.36(2)
		N–B ^a	1.53(4)
I(1)–U–O(1)	86.8(5)	N(1)–U–N(3)	71.8(6)
I(1)–U–N(1)	117.7(5)	N(1)–U–N(4)	73.0(6)
I(1)–U–N(3)	78.4(5)	N(1)–U–N(6)	72.6(6)
I(1)–U–N(4)	75.6(5)	N(2)–U–N(3)	70.5(6)
I(1)–U–N(5)	79.7(5)	N(2)–U–N(5)	121.7(6)
O(1)–U–N(2)	72.4(7)	N(2)–U–N(6)	75.4(6)
O(1)–U–N(3)	85.7(6)	N(3)–U–N(4)	118.3(7)
O(1)–U–N(5)	75.8(7)	N(4)–U–N(5)	72.1(8)
O(1)–U–N(6)	108.3(6)	N(4)–U–N(6)	71.9(7)
N(1)–U–N(2)	70.3(6)	N(5)–U–N(6)	70.0(7)
U–O(1)–C(1)	173(1)	C(2)–C(3)–C(4)	113(2)
O(1)–C(1)–C(2)	110(2)	C(3)–C(4)–I(2)	114(2)
C(1)–C(2)–C(3)	111(2)	N–B–N ^a	111(2)

^a Mean value for the pyrazolyl rings.

packing model [17], the evaluation of the steric crowding about the metal in many structurally characterized compounds led to a new definition of steric coordination number [18]. According to this model, the (HBpz₃)[−] and [C₅H₃-1,3(SiMe₃)₂][−], although being formally six-electron donors, have different steric coordination numbers 2.90 and 2.60 respectively. In compound **2** the U–O(1) bond length is 2.012(14) Å and the U–O(1)–C(1) bond angle is 173(1)°. This very short U–O bond and the almost linear U–O–C bond angle are comparable with distances and bond angles previously found in [UCl(O^tBu)(HBpz₃)₂] (2.032(5) Å, 165(1)°) and [UCl(OC₆H₅)(HBpz₃)₂] (2.076(12) Å, 165(1)°) [15], and provide some evidence of π-bonding between U and O. For uranium alkoxides, partial multiple-bond character in the metal–oxygen bond has been suggested as an explanation for such short lengths and large M–O–C angles [19]. The values found for compound **2** also compare quite well with the U–O bond lengths and with the U–O–C angles found for the alkoxides [(triox)U(BH₄)₃(THF)] (U–O 1.97(1) Å and U–O–C 178.6(5)°) and [(triox)₃U(BH₄)] (U–O_{aver} 2.07 Å and U–O–C_{aver} 170°), molecules in which strong

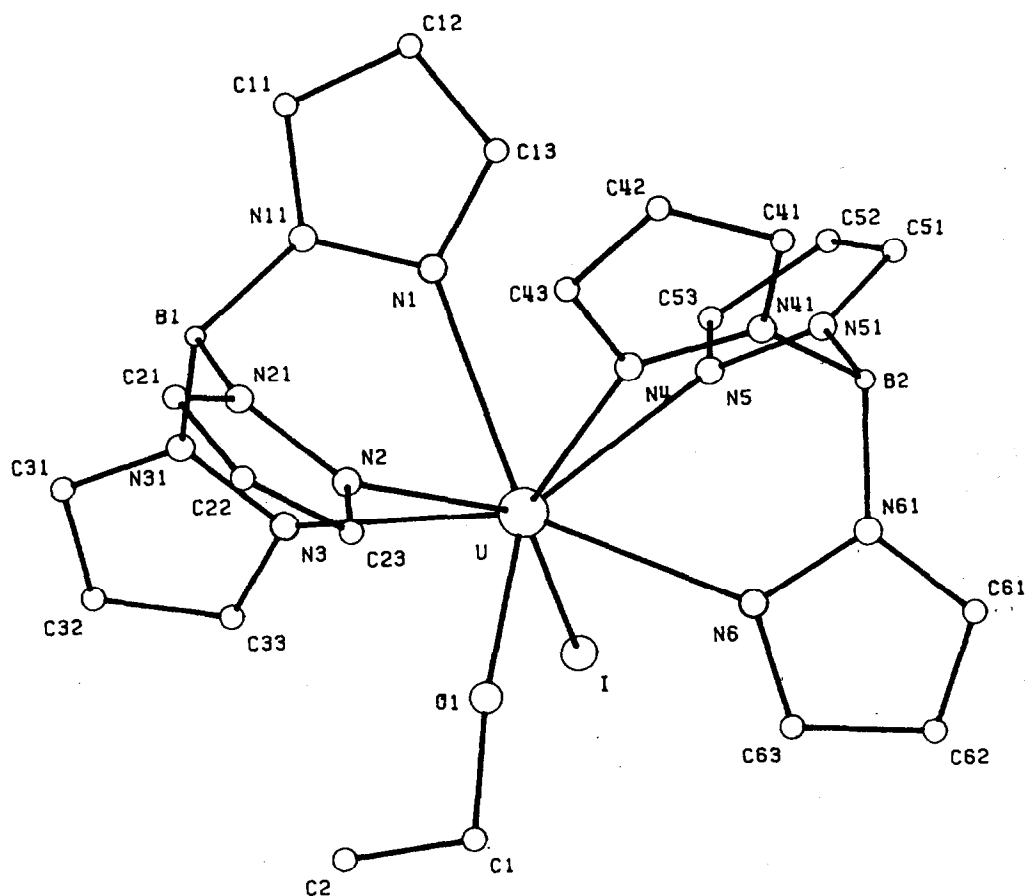
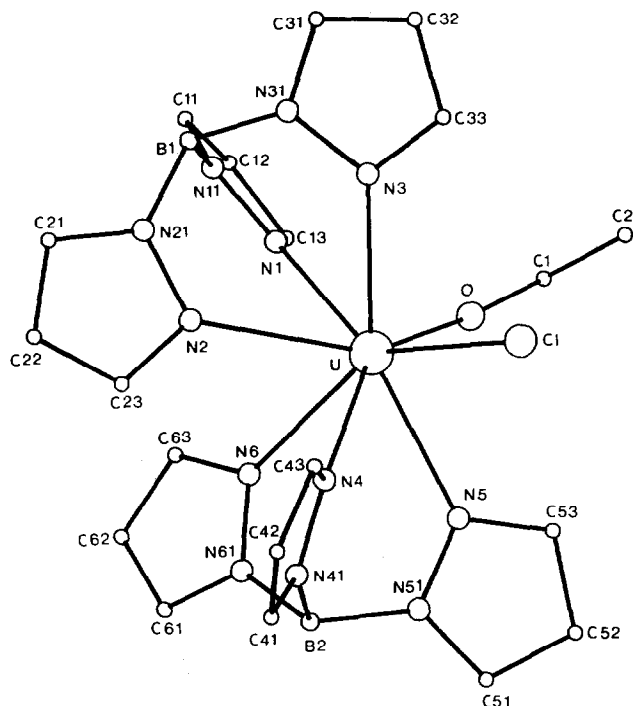


Fig. 2. PLUTO view of [U(OCH₂H₅)(HBpz₃)₂].

Fig. 3. PLUTO view of $[UCl(OC_2H_5)(HBpz_3)_2]$.

π -bonding between the U and the O atoms has also been suggested [20].

The dimensions of the two tridentate $(HBpz_3)^-$ bonded to the uranium atom are essentially the same and are comparable with those observed in other actinide poly(pyrazolyl)borates previously characterized. The N–U–N angles are similar and average $71(1)^\circ$. The closest interligand contacts are 3.15 and 3.16 Å for N(4)...C(13) and N(2)...C(63), respectively. Each of the pyrazolyl rings of the two ligands is approximately planar.

3.2. Crystal structures of $[UI(OC_2H_5)(HBpz_3)_2]$ (3) and $[UCl(OC_2H_5)(HBpz_3)_2]$ (4)

The PLUTO drawings of the two molecules are shown in Figs. 2 and 3 respectively and selected bond distances and angles are listed in Tables 7 and 8.

Both structures consist of discrete molecules in which the U atom is 8-coordinate in a distorted SAP geometry. In 3 the "square" face, N(2) N(4) N(6) O, is nearly planar (root-mean-square deviation of 0.0214 Å; $\delta = 2.2^\circ$) whereas the N(3) N(1) N(5) I face is quite folded with a δ value of 13.0° . In 4, the face formed by N(2) N(3) Cl N(4) is nearly planar (root-mean-square deviation of 0.0088 Å; $\delta = 0.9^\circ$), and the other "square" face made up of N(1) N(6) N(5) O is distorted from planarity ($\delta = 14.3^\circ$). The loss of planarity of one of the "square faces" in both compounds show that the distortion of the SAP is along the geometric pathway towards the BCTP.

Table 7

Selected bond lengths (Å) and bond angles ($^\circ$) for $[UI(OC_2H_5)(HBpz_3)_2]$

U–I	3.135(4)	O–C(1)	1.50(2)
U–O	2.027(9)	C(1)–C(2)	1.31(2)
U–N(1)	2.637(12)		
U–N(2)	2.530(13)	C–C ^a	1.38(4)
U–N(3)	2.584(13)	C–N ^a	1.34(1)
U–N(4)	2.587(12)	N–N ^a	1.36(2)
U–N(5)	2.615(13)	N–B ^a	1.54(2)
U–N(6)	2.538(13)		
I–U–O	85.7(4)	N(1)–U–N(5)	71.3(4)
I–U–N(3)	77.7(3)	N(2)–U–N(3)	70.0(4)
I–U–N(5)	74.5(3)	N(2)–U–N(4)	72.9(4)
I–U–N(6)	83.3(3)	N(4)–U–N(5)	73.5(4)
O–U–N(2)	74.7(4)	N(4)–U–N(6)	70.8(4)
O–U–N(3)	86.0(4)	N(5)–U–N(6)	70.4(4)
O–U–N(6)	75.5(5)	I–U–N(1)	113.0(3)
N(1)–U–N(2)	74.0(4)	O–U–N(4)	110.4(4)
N(1)–U–N(3)	72.1(4)	N(2)–U–N(6)	120.2(4)
N(1)–U–N(4)	71.2(4)	N(3)–U–N(5)	119.6(4)
U–O–C(1)	171.9(14)	O–C(1)–C(2)	101(3)
N–B–N ^a	109(1)		

^a Mean value for the pyrazolyl rings.

The two compounds show very similar U–O bond lengths (2.027(9) and 2.028(9) Å respectively) and U–O–C angles ($172(1)^\circ$ and $171(1)^\circ$ respectively), which compare well with the values found in compound 2, and also provide evidence of π -bonding between the U and the O.

The U–N bond lengths (average 2.58(4) Å and 2.59(3) Å) are comparable to those in compound 2 and are in the range observed in other poly(pyrazolyl) borates. The U–I bond distance in compound 3 (3.135(4) Å) is the same as the corresponding value in compound 2. The U–Cl distance in 4 (2.690(5) Å) is

Table 8

Selected bond lengths (Å) and bond angles ($^\circ$) for $[UCl(OC_2H_5)(HBpz_3)_2]$

U–Cl	2.690(5)	O–C(1)	1.428(14)
U–O	2.028(9)	C(1)–C(2)	1.38(2)
U–N(1)	2.595(12)		
U–N(2)	2.640(11)	C–C ^a	1.38(2)
U–N(3)	2.565(11)	C–N ^a	1.34(1)
U–N(4)	2.556(12)	N–N ^a	1.36(1)
U–N(5)	2.569(12)	N–B ^a	1.54(2)
U–N(6)	2.602(11)		
Cl–U–O	87.9(3)	N(2)–U–N(3)	73.1(4)
Cl–U–N(3)	74.9(3)	N(2)–U–N(4)	69.2(4)
Cl–U–N(4)	76.2(3)	N(2)–U–N(6)	71.3(4)
Cl–U–N(5)	79.6(3)	N(4)–U–N(5)	69.2(4)
O–U–N(1)	74.0(4)	N(4)–U–N(6)	75.0(4)
O–U–N(3)	91.4(4)	N(5)–U–N(6)	70.2(4)
O–U–N(5)	77.8(4)	N(2)–U–Cl	117.2(3)
N(1)–U–N(2)	70.6(4)	N(3)–U–N(4)	113.2(4)
N(1)–U–N(3)	70.1(4)	N(1)–U–N(5)	128.6(4)
N(1)–U–N(6)	76.1(4)	N(6)–U–O	104.0(4)
U–O–C(1)	171.3(8)	O–C(1)–C(2)	116(1)
N–B–N ^a	109(2)		

^a Mean value for the pyrazolyl rings.

comparable with the value of 2.697(2) Å in [UCl(O^tBu)(HBpz₃)₂] and of 2.682(6) Å in [UCl(OC₆H₅)(HBpz₃)₂] but is longer than the U–Cl bond distance (2.63(1) Å) found in [UCl₂(HBpz₃)₂] [1c,15]. The X–U–O bond angles (X = I, Cl) are 85.7(4)° and 87.9(3)° for **3** and **4** respectively, and are comparable with the value of 86.8(5)° found in **2**. Based on structurally characterized compounds containing the moiety “M(HBpz₃)₂” [1c,15,21] we can say that the angle X–U–Y does not change significantly with the bulkiness of X and Y, contrary to what has been observed for compounds of the type [UXY(C₅Me₅)₂] (X = Y = Cl, 97.9(4)°; X = Cl and Y = pz, 103.2°) [22,23] and this is also probably due to the different sizes and shapes of the (HBpz₃)[−] and (C₅Me₅)[−], as shown by their steric coordination numbers, 2.90 and 2.49, respectively [18].

Due to the disorder of the ethoxide carbon atoms in **3**, bond distances and angles involving these atoms are probably not as accurate as indicated (see experimental section).

The dimensions of the (HBpz₃)[−] are the same in both compounds and compare well with the values found in compound **2**. The mean bite distance between the coordinated nitrogen atoms of (HBpz₃)[−] is 3.03 and 3.02 Å for compound **3** and **4**, respectively, compared to 3.00 Å for compound **2**. The N–U–N angles average 72(1) and 71(2)° for compounds **3** and **4**, respectively. There are a few short interligand contacts: in compound **3**, 3.15 and 3.08 Å for N(5)...C(13) and N(2)...C(43), 3.27 and 3.35 Å for C(23)...C(43) and C(13)...C(53); in compound **4**, 2.95 and 3.20 Å for N(2)...N(4) and N(1)...C(63). For both compounds the pyrazolyl rings of the (HBpz₃)[−] are approximately planar.

3.3. Behaviour in solution of compounds containing the moiety “M(HBpz₃)₂”

For yttrium, lanthanides and actinides several compounds containing the moiety “M(HBpz₃)₂” have been previously synthesized and for some of them X-ray crystallographic analysis as well as variable temperature ¹H NMR studies have been undertaken [1,15,21, 24–29]. These compounds crystallize as eight-coordinate species and almost all of them display a square antiprismatic geometry (SAP) more or less distorted in the direction of the bicapped trigonal prism (BCTP) or the dodecahedron (DD). Only for [Yb(η²HBpz₃)(HBpz₃)₂] and [Ce(acac)(HBpz₃)₂] is the coordination geometry around the metal best described as BCTP.

Excluding [Yb(η²HBpz₃)(HBpz₃)₂], all the compounds of this family show a dynamic behaviour in variable-temperature ¹H NMR experiments. Normally either at room temperature or in a few cases above than 300 K, they show only one set of signals for the protons of the pyrazolyl rings, which is consistent with

the solid state structures normally found (SAP, BCTP), provided there is a rapid dynamic process on the NMR time scale. There is evidence that this dynamic process is slowed down on lowering the temperature, but only for [Yb(η²HBpz₃)(HBpz₃)₂] and for several uranium compounds was it possible to obtain limiting static spectra with a pattern which was consistent with the structures found in the solid state [15,21,25,27–29]. A possible mechanism for the fluxionality of the eight-coordinate complexes containing the moiety “M(HBpz₃)₂” is the interconversion of the most common eight-coordinate polyhedra SAP, DD and BCTP [30,31].

As we have shown, **2**, **3** and **4** have solid state structures which compare with others found for this family of compounds and at 300 K they also show a ¹H NMR spectra consistent with dynamic behaviour, as only one set of resonances is observed for the protons of the pyrazolyl rings (Table 5). No X-ray structural analysis has been undertaken for **1** until now but in this compound the uranium is probably also eight-coordinate by the two tridentate HBpz₃ ligands and by the two iodides, with a SAP geometry. For **1**, at 300 K (Table 5) the ¹H NMR spectrum shows only three signals of equal intensity for the protons of the pyrazolyl rings, consistent with the magnetic equivalence of these rings, certainly due to dynamic behaviour in solution. This is similar to what has been observed for other compounds of this family.

On comparison with the diamagnetic analogue, [ThCl₂(HBpz₃)₂], we observed that for **1** the resonances due to the H(3) and H(4) protons of the pyrazolyl rings are shifted to lower field and the resonance due to the H(5) protons is shifted to higher field. This is exactly what we had observed before for the analogous paramagnetic compound [UCl₂(HBpz₃)₂] (Table 5). However, on comparison of **1** with [UCl₂(HBpz₃)₂] the resonances appear less shifted relative to those of the diamagnetic compound. As we are dealing with the same metal and with the same stabilizing ligands this difference is certainly due to the nature of the halide.

For compound **1** we did not observe at room temperature any signal due to the protons coordinated to the boron atoms, though these could easily be observed in the ¹H NMR spectrum of [UCl₂(HBpz₃)₂]. A line-broadening of this resonance probably makes it indistinguishable from the base line, because this is a low-intensity resonance that is normally a broad multiplet due to the coupling with the boron. On comparing **1** with [UCl₂(HBpz₃)₂] we observed for all the resonances of the pyrazolyl rings a line broadening accompanied by a loss of multiplet structure (Table 5). Only when one iodide is replaced by one alkoxide, as in compounds **2**, **3** and **6** (Table 5) do we detect at high field a very broad multiplet resonance, which by its structure and intensity can be attributed to the protons coordinated to boron. However, when one iodide in **1**

is replaced by an alkoxide, as in compounds **2**, **3**, and **6**, the resonances due to the protons of the pyrazolyl rings and specially the resonances due to the alkoxide groups are much more shifted relative to the diamagnetic region than are the corresponding resonances in the chloride compounds **4** and $[\text{UCl}(\text{OC}_6\text{H}_5)(\text{HBpz}_3)_2]$ (Table 5).

4. Final remarks

As we have shown before [11], uranium tetraiodide, due to its Lewis acidity, opens the THF leading to the formation of iodobutoxide species, which is a disadvantage for the synthesis of compounds of the type UI_2L_2 ($\text{L} = \text{HBpz}_3$). This type of compounds can be straightforwardly synthesized in CH_2Cl_2 , in spite of the insolubility of UI_4 in this solvent.

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