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Synthesis and crystal structure of $[U(\eta\text{-}C_5Me_5)_2(OC_4H_8)_2][BPh_4]$, the first cationic cyclopentadienyl compound of uranium(III)

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Abstract

The mixed amide complexes $[U(NEt_2)_2(N\{SiMe_3\}_2)_2]$ and $[U(\eta\text{-}C_8H_8)(NEt_2)(N\{SiMe_3\}_2)]$ reacted in tetrahydrofuran (THF) with NEt_3HBPh_4 to give the cations $[U(NEt_2)(N\{SiMe_3\}_2)_2(THF)_x]^+$ and $[U(\eta\text{-}C_8H_8)(N\{SiMe_3\}_2)(THF)_x]^+$. The bis(trimethylsilyl) amide complex $[U(\eta\text{-}C_5Me_5)_2(N\{SiMe_3\}_2)]$ was inert towards NEt_3HBPh_4 but its treatment with NH_4BPh_4 afforded the cationic uranium(III) compound $[U(\eta\text{-}C_5Me_5)_2(THF)_2][BPh_4]$, the crystal structure of which has been determined.

Keywords: Uranium (III); Cation; Cyclopentadienyl

1. Introduction

Protonolysis of metal dialkylamide complexes by means of the ammonium salt NEt_3HBPh_4 represents an efficient and practical synthesis of cationic compounds.

$$[M]\text{–}NR_2 + NEt_3HBPh_4 \rightarrow [M][BPh_4] + NEt_3 + NR_2H \quad (1)$$

The reaction in Eq. (1) served to prepare the Group 4 metal cations $[M(NMe_2)_3(THF)_x]^+$ (M = Ti and $x = 1$; M = Zr or Hf and $x = 2$) and $[M(\eta\text{-}C_5H_5)_2(NMe_2)(NC_5H_5)]^+$ (M = Zr or Hf) [1]. By this way, a series of cationic uranium(IV) complexes were synthesized from $[U(NEt_2)_4]$ and various cyclopentadienyl and cyclooctatetraene amide precursors [2,3]; a unique example of a uranium(V) cation, $[U(\eta\text{-}C_8H_8)(NEt_2)_2(THF)]^+$, was also isolated [4]. The very rare uranium(III) cations so far reported have been prepared either by heterolytic cleavage of a metal–halogen bond [5] or protonolysis of a U–C [6] or U–H bond [7]. It was then interesting to assess the potential of the reaction in Eq. (1) in the preparation of new cationic complexes of uranium(III). Here we report on the synthesis and X-ray crystal structure of $[U(cp*)_2(THF)_2][BPh_4]$ ($cp* = \eta\text{-}C_5Me_5$), the first cationic metallocene compound of uranium(III). The protonolysis reaction of $[U(cp*)_2(N\{SiMe_3\}_2)]$ revealed the distinct behaviour of the bis(trimethylsilyl) amide ligand.

2. Results and discussion

Application of the reaction in Eq. (1) to the synthesis of cationic uranium(III) compounds is actually quite restricted because of the very few neutral amide precursors in this oxidation state. Only three have been reported: the bis(trimethylsilyl) amide derivatives $[(\{Me_3Si\}_2N)_4U_2(\mu\text{-}N\{H\}\{mesityl\})_2]$ [8], $[U(N\{SiMe_3\}_2)_3]$ [9] and $[U(cp*)_2(N\{SiMe_3\}_2)]$ [10]. The superiority of the more polarizable $N(SiMe_3)_2$ ligand over the dialkylamido group NR_2 for stabilizing metal complexes in low oxidation states is well documented [11]. The other advantage of the bis(trimethylsilyl) amide ligand is to prevent, by its steric hindrance, the dimerization of the low valent metal species and their subsequent ligand exchange and disproportionation reactions. Our own attempts to isolate dialkylamide complexes of uranium(III) by reduction of cationic pre-

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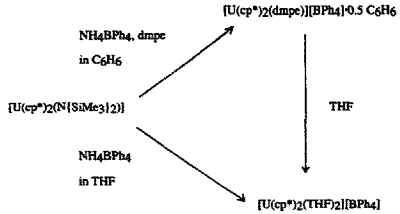

Scheme 1. Synthesis of the cationic uranium(III) compounds.

cursors of the type $[\{U^{IV}\}(NR_2)]^+$ were unsuccessful; only tetravalent uranium products could be identified (see Section 3). In particular, treatment of $[U(NEt_2)_3][BPh_4]$ with sodium amalgam afforded $[U(NEt_2)_4]$ with total recovery of the NEt_2 ligands, indicating that the putative $[U(NEt_2)_3]$ would readily disproportionate, according to Eq. (2); the trivalent species was not detected by NMR or UV–visible spectroscopy.

$$4[U(NEt_2)_3] \rightarrow 3[U(NEt_2)_4] + U^0 \quad (2)$$

This disproportionation reaction would be facilitated by the ability of $[U(NEt_2)_3]$ to adopt, like $[U(NEt_2)_4]$ [12], a dimeric structure. The instability of the U(III) dialkylamide complexes may be compared with that of some samarium(II) analogues, which have been studied recently [13]; for example, $[\{(Cy_2N)_2Sm(\mu\text{-}Cl)(THF)\}_2]$ ($Cy = C_6H_{11}$) was found to react with lithium naphthalide to give metallic samarium and $[Sm(NCy_2)_3(THF)]$.

In contrast to the dialkylamide complexes of uranium and Group 4 metals which were readily protonated at 20 °C with NEt_3HBPh_4, $[U(cp*)_2(N\{SiMe_3\}_2)]$ was inert towards this ammonium salt whereas $[U(N\{SiMe_3\}_2)_3]$ was slowly transformed into not yet identified products. The lesser reactivity of the bis(trimethylsilyl) amide ligand was also evident in the mixed NEt_2–$N(SiMe_3)_2$ uranium(IV) derivatives $[U(NEt_2)_2(N\{SiMe_3\}_2)_2]$ and $[U(\eta\text{-}C_8H_8)(NEt_2)(N\{SiMe_3\}_2)]$ [14]. In the presence of NEt_3HBPh_4, the latter were readily transformed in THF, according to Eqs. (3) and (4), into the cations $[U(NEt_2)(N\{SiMe_3\}_2)_2(THF)_x]^+$ and $[U(\eta\text{-}C_8H_8)(N\{SiMe_3\}_2)(THF)_x]^+$, with liberation of NEt_2H (NMR experiments).

$$[U(NEt_2)_2(N\{SiMe_3\}_2)_2] + NEt_3HBPh_4 \rightarrow [U(NEt_2)(N\{SiMe_3\}_2)_2(THF)_x][BPh_4] + NEt_3 + NEt_2H \quad (3)$$

$$[U(\eta\text{-}C_8H_8)(NEt_2)(N\{SiMe_3\}_2)] + NEt_3HBPh_4 \rightarrow [U(\eta\text{-}C_8H_8)(N\{SiMe_3\}_2)(THF)_x][BPh_4] + NEt_3 + NEt_2H \quad (4)$$

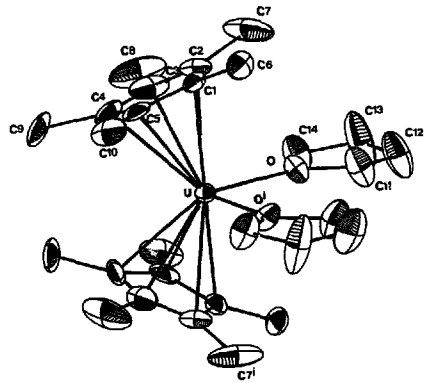

Fig. 1. ORTEP drawing of the cation $[U(cp*)_2(THF)_2]^+$. Atoms labelled i are related to those unlabelled by the two-fold axis.

This remarkable selectivity can be easily explained by the steric and electronic effects of the $SiMe_3$ groups which impede the attack of the acidic reagent onto the nitrogen atom of the bis(trimethylsilyl) amide ligand.

Protonolysis of $[U(cp*)_2(N\{SiMe_3\}_2)]$ could be achieved by replacing NEt_3HBPh_4 with NH_4BPh_4 (Scheme 1); the greater reactivity of this latter can be accounted for by its smaller size and its more important acidic character. The U(III) compound reacted in benzene with NH_4BPh_4 in the presence of dimethylphosphinoethane (dmpe) to afford the brown cationic product $[U(cp*)_2(dmpe)][BPh_4]\cdot 0.5C_6H_6$ which crystallized from this solvent (78% yield). The diphosphine ligand was readily displaced by THF, giving $[U(cp*)_2(THF)_2][BPh_4]$, which was directly obtained by protonolysis of the bis(trimethylsilyl) amide precursor in tetrahydrofuran and was isolated as green microcrystals in 79% yield.

The solid state structure of $[U(cp*)_2(THF)_2][BPh_4]$ was determined by X-ray diffraction analysis. The crystals are composed of discrete cation–anion pairs. The

Table 1
Selected bond distances (Å) and angles (deg) with estimated standard deviations for $[U(cp*)_2(THF)_2][BPh_4]$

Bond distances			
U–O	2.511(8)	U–C(1)	2.738(9)
U–C(2)	2.75(1)	U–C(3)	2.68(2)
U–C(4)	2.72(2)	U–C(5)	2.73(1)
<U–C>	2.72(3)	U–cp* [a]	2.46(1)
Bond angles			
O–U–O^i	95.2(4)	cp*–U–O	104.0(5)
cp*–U–cp*^{i}	134.2(5)		

[a] cp* is the centroid of the cyclopentadienyl ring. Symmetry code i: $-x, y, 1/2-z$.

Table 2
Structural parameters of the $U(cp*)_2$ fragment in complexes in the oxidation states +3, +4 and +5

Compound	cp*–U–cp* [a] (deg)	<U–C> (Å)	<U–cp*> (Å)
$[U(cp*)_2(THF)_2][BPh_4]$	134.2(5)	2.72(4)	2.46(1)
$[U(cp*)_2(BH_4)_2]$	133(1)	2.74(3)	2.47(5)
$[U(cp*)_2(NEt_2)_2][BPh_4]$	132.6(1)	2.76(2)	2.49(1)

[a] cp* is the centroid of the cyclopentadienyl ring.

BPh_4 anion displays the expected geometry; an ORTEP [15] drawing of the cation is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. The complex is isostructural with the samarium analogue $[Sm(cp*)_2(THF)_2][BPh_4]$ [16] and it is not necessary to go back to the comments previously presented. The U–C and U–O bond distances are longer, by ca. 0.05 Å, than the Sm–C and Sm–O bond lengths; this value can be compared to the 0.07 Å difference between U^{3+} and Sm^{3+} in the same coordination [17]. However, it is noteworthy that the geometry of the $U(cp*)_2$ fragment is quite similar to that found in the complexes $[U(cp*)_2(BH_4)_2]$ [18] and $[U(cp*)_2(NEt_2)_2][BPh_4]$ [19] which are respectively in the +4 and +5 oxidation states. The geometrical parameters reported in Table 2 confirm that the metal valency cannot be defined by such structural criteria [20].

3. Experimental details

3.1. General methods

All preparations and reactions were carried out under argon (< 5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use; THF-d_8 was dried over Na–K alloy.

Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The ^1H NMR spectra were recorded on a Bruker WP 60 (FT) instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0); the spectra are described in Table 3.

The commercial reagents were dried by standard methods before use. NEt_3HBPh_4 and NH_4BPh_4 were prepared in water by mixing $NaBPh_4$ with NEt_3HCl or NH_4Cl; the white powder which precipitated was filtered off, washed successively with hot water and diethyl ether and dried under vacuum. The uranium compounds $[U(NEt_2)_4]$ [12], $[U(NEt_2)_3][BPh_4]$ [2], $[U(NEt_2)Cl_2(THF)_2][BPh_4]$ [2], $[U(\eta\text{-}C_8H_8)(NEt_2)(THF)_2][BPh_4]$ [3], $[U(\eta\text{-}C_8H_8)(NEt_2)(N\{SiMe_3\}_2)]$ [14] and $[U(cp*)_2(N\{SiMe_3\}_2)]$ [10] have been synthesized by published methods.

3.2. Attempted reductions of cationic uranium(IV) dialkylamide compounds

3.2.1. $[U(NEt_2)_3][BPh_4]$

An NMR tube was charged with the cationic complex (10.0 mg, 0.013 mmol) and 2% Na(Hg) (15.0 mg, 0.013 mmol Na) in THF-d_8 (0.4 ml). The tube was first immersed in an ultrasound bath (60 W, 40 kHz) for 20 min and was then kept at 20 °C for 2 h. The spectrum showed that the cation was converted into $[U(NEt_2)_4]$; integration of the signals indicated that the NEt_2 ligands were totally recovered.

3.2.2. $[U(NEt_2)Cl_2(THF)_2][BPh_4]$

An NMR tube was charged with the cationic complex (10.0 mg, 0.022 mmol) and 2% Na(Hg) (25.4 mg, 0.022 mmol Na) in THF-d_8 (0.4 ml). After the same treatment as before, the spectrum showed that the cation was converted into $[U(NEt_2)_2Cl_2]$ and integration of the signals indicated that the NEt_2 ligands were totally recovered.

3.2.3. $[U(\eta\text{-}C_8H_8)(NEt_2)(THF)_2][BPh_4]$

An NMR tube was charged with the cationic complex (9.7 mg, 0.011 mmol) and 2% Na(Hg) (12.7 mg, 0.011 mmol Na) in THF-d_8 (0.4 ml). After the same treatment as before, green microcrystals of $[U(\eta$-

Table 3
^1H NMR spectra of the compounds [a]

Compound	^1H NMR data
$[U(NEt_2)_2(N\{SiMe_3\}_2)_2]$	13.7 (8H, CH_2CH_3); 5.1 (12H, CH_2CH_3); −3.52 (36H, $SiMe_3$)
$[U(NEt_2)(N\{SiMe_3\}_2)_2(THF)_2][BPh_4]$	38.4 (4H, CH_2CH_3); 5.9 (26H, CH_2CH_3 and Ph); −4.67 (36H, $SiMe_3$)
$[U(\eta\text{-}C_8H_8)(N\{SiMe_3\}_2)(THF)_2][BPh_4]$	−32.47 (8H, C_8H_8); 6.0 (20H, Ph); 1.98 (18H, $SiMe_3$)
$[U(cp*)_2(THF)_2][BPh_4]$	5.8 and 5.3 (12H + 8H, Ph); 0.1 (30H, $w_{1/2}$ = 50 Hz, cp*)

[a] At 30 °C in THF-d_8, δ relative to TMS. When not specified, the signals are singlets with half-height widths between 10 and 30 Hz.

$C_8H_8)_2$] were deposited and the spectrum showed that the cation was also converted into [U(η-C_8H_8)(NEt_2)$_2$(THF)].

3.3. Synthesis of [U(NEt_2)$_2$(N{$SiMe_3$}$_2$)$_2$]

A 50 ml round-bottomed flask was charged with [U(NEt_2)$_4$] (727 mg, 1.38 mmol) in toluene (20 ml) and N($SiMe_3$)$_2$H (1.75 ml, 8.29 mmol) was introduced via a syringe. The green solution was heated at 85 °C for 60 h and turned yellow. After evaporation to dryness, the residue was treated again in toluene (20 ml) with N($SiMe_3$)$_2$H (1.75 ml); the mixture was heated at 85 °C for 24 h. After evaporation, the residue was extracted with pentane (20 ml). The solvent was evaporated off, leaving the product as an orange sticky powder (658 mg, 68%). Anal. Found: C, 34.03; H, 7.97; N, 7.84. $C_{20}H_{56}N_4Si_4U$ calc.: C, 34.17; H, 8.03; N, 7.97%.

3.4. Protonolysis of [U(NEt_2)$_2$(N{$SiMe_3$}$_2$)$_2$] and [U(η-C_8H_8)(NEt_2)(N{$SiMe_3$}$_2$)]

(a) An NMR tube was charged with [U(NEt_2)$_2$(N{$SiMe_3$}$_2$)$_2$] (6.9 mg, 0.010 mmol) and

Table 4
Crystallographic data and details for [U(cp*)$_2$(THF)$_2$][BPh_4]

Crystal data	
Formula	$C_{52}H_{66}BO_2U$
M	971.95
Crystal dimensions (mm^3)	0.50×0.45×0.40
Colour	Green
Crystal system	Monoclinic
Space group	$P2/c$
a (Å)	10.589(4)
b (Å)	14.245(6)
c (Å)	16.291(8)
β (deg)	107.07(3)
V (Å^3)	2349(3)
Z	2
D_{calc} (g cm^{-3})	1.374
μ(Mo Kα) (cm^{-1})	33.108
F(000)	982
Data collection	
θ limits (deg)	1, 20
Scan type	$\omega-2\theta$
Scan width	$0.8+0.35\tan\theta$
Range of absolute transmission	0.818, 0.999
Range of h,k,l	−11 to 0, 0 to 13, −15 to 15
Number of reflections collected	
total	2568
unique	2246
with $I>3\sigma(I)$	1807
Number of parameters	254
$R=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0.035
$R_w=[\Sigma w\|\|F_o\|-\|F_c\|\|^2/\Sigma w(\|F_o\|)^2]^{1/2}$	0.045
Maximum residual electron density (e$^-$ Å^{-3})	0.532

Table 5
Fractional atomic coordinates, thermal parameters and their estimated standard deviations for [U(cp*)$_2$(THF)$_2$][BPh_4]

Atom	x	y	z	B (Å^2) [a]
U	0.000	−0.16360(4)	0.250	5.01(1)
O	0.1679(7)	−0.2825(6)	0.3275(4)	8.6(2)
C(1)	0.0564(9)	−0.1634(6)	0.0964(5)	6.7(2)
C(2)	0.178(1)	−0.1486(9)	0.1574(6)	9.3(3)
C(3)	0.181(1)	−0.071(1)	0.1952(7)	14.2(4)
C(4)	0.078(1)	−0.0199(8)	0.1664(7)	13.0(3)
C(5)	−0.0170(9)	−0.0789(9)	0.0969(5)	9.0(3)
C(6)	0.012(1)	−0.2459(9)	0.0356(6)	10.6(4)
C(7)	0.291(1)	−0.221(2)	0.172(1)	20.5(7)
C(8)	0.313(1)	−0.035(2)	0.263(1)	22.4(7)
C(9)	0.030(2)	0.084(1)	0.1612(9)	26.0(5)
C(10)	0.155(1)	0.055(1)	0.9661(8)	15.5(4)
C(11)	0.156(2)	−0.384(1)	0.315(1)	15.0(6)
C(12)	0.275(2)	−0.425(1)	0.379(1)	18.0(7)
C(13)	0.361(2)	−0.356(1)	0.417(2)	23.1(9)
C(14)	0.296(1)	−0.266(1)	0.3927(8)	11.9(4)
C(15)	0.4635(9)	0.2554(7)	0.3260(6)	7.2(3)
C(16)	0.378(1)	0.2875(9)	0.3687(8)	11.1(4)
C(17)	0.348(2)	0.243(1)	0.432(1)	15.7(6)
C(18)	0.402(2)	0.164(1)	0.455(1)	17.1(6)
C(19)	0.499(1)	0.1191(9)	0.4223(8)	12.6(4)
C(20)	0.531(1)	0.1701(7)	0.3520(8)	10.0(3)
C(21)	0.375(1)	0.3819(8)	0.1959(7)	8.1(3)
C(22)	0.404(2)	0.468(1)	0.162(1)	14.1(5)
C(23)	0.294(2)	0.527(1)	0.107(1)	20.2(6)
C(24)	0.163(2)	0.483(1)	0.0926(9)	17.5(6)
C(25)	0.131(2)	0.408(1)	0.129(1)	16.0(5)
C(26)	0.242(1)	0.3495(9)	0.182(1)	12.9(4)
B	0.500	0.3191(9)	0.250	5.9(4)

[a] $B_{eq}=(4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$.

NEt_3HBPh_4 (4.1 mg, 0.010 mmol) in THF-d_8 (0.4 ml). After 10 min at 20 °C, the spectrum showed that the compound was totally transformed into the cation [U(NEt_2)(N{$SiMe_3$}$_2$)$_2$(THF)$_x$]$^+$, with liberation of NEt_3 and NEt_2H (one equivalent each).

(b) An NMR tube was charged with [U(η-C_8H_8)(NEt_2)(N{$SiMe_3$}$_2$)] (10.0 mg, 0.017 mmol) and NEt_3HBPh_4 (7.3 mg, 0.017 mmol) in THF-d_8 (0.4 ml). After 10 min at 20 °C, the spectrum showed that the compound was totally transformed into the cation [U(η-C_8H_8)(N{$SiMe_3$}$_2$)(THF)$_x$]$^+$, with liberation of NEt_3 and NEt_2H (one equivalent each).

3.5. Synthesis of [U(cp*)$_2$(dmpe)][BPh_4] · 0.5C_6H_6

A 50 ml round-bottomed flask was charged with [U(cp*)$_2$(N{$SiMe_3$}$_2$)] (556 mg, 0.83 mmol) and NH_4BPh_4 (259 mg, 0.77 mmol) in benzene (30 ml) and dmpe (155 μl, 0.93 mmol) was introduced via a microsyringe. The mixture was heated at 80 °C for 4 days and the brown microcrystalline product which was deposited was filtered off, washed with benzene (20 ml) and dried under vacuum (610 mg, 78%). Anal. Found: C, 62.28;

H, 6.71; P, 5.86. $C_{53}H_{69}BP_2U$ calc.: C, 62.60; H, 6.84; P, 6.09%.

3.6. Synthesis of $[U(cp*)_2(THF)_2][BPh_4]$

A 50 ml round-bottomed flask was charged with $[U(cp*)_2(N\{SiMe_3\}_2)]$ (150 mg, 0.22 mmol) and NH_4BPh_4 (70 mg, 0.21 mmol) and THF (20 ml) was condensed in under vacuum at −78 °C. The reaction mixture was stirred for 16 h at 20 °C and after filtration, the brown solution was evaporated to dryness. An orange impurity was eliminated by washing the residue with diethyl ether (3 × 15 ml) and the green product was dried under vacuum (160 mg, 79%). Orange microcrystals suitable for X-ray diffraction analysis were obtained by crystallization from THF–pentane. Anal. Found: C, 64.04; H, 6.75. $C_{52}H_{66}BO_2U$ calc.: C, 64.26; H, 6.84%.

3.7. X-ray crystal structure of $[U(cp*)_2(THF)_2][BPh_4]$

A selected single crystal was introduced into a thin-walled Lindemann glass tube in the glove box. Data were collected on an Enraf–Nonius CAD-4 diffractometer equipped with a graphite monochromator [λ(Mo Kα) = 0.70073 Å]. The cell parameters were obtained by a least squares refinement of the setting angles of 25 reflections with θ between 8 and 12°. Three standard reflections were measured after every hour; a decay was observed (9.8% in 35 h) and linearly corrected. The data were corrected for Lorentz polarization effects and absorption [21]. The structure was solved by the heavy-atom method and refined by full matrix least squares on F with anisotropic thermal parameters; H atoms were not introduced. All calculations were performed on a Vax 4000–200 computer with the Enraf–Nonius MolEN system [22]. Analytical scattering factors for neutral atoms were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion [23]. Crystallographic data are given in Table 4 and final positional parameters in Table 5.

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