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Arene uranium borohydrides: synthesis and crystal structure of $(\eta\text{-C}_6\text{Me}_6)\text{U}(\text{BH}_4)_3$

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Abstract

Thermal decomposition of $\text{U}(\text{BH}_4)_4$ (I) in mesitylene afforded red crystals of $(\eta\text{-mesitylene})\text{U}(\text{BH}_4)_3$ (II); displacement of the arene ligand of II by hexamethylbenzene gave $(\text{C}_6\text{Me}_6)\text{U}(\text{BH}_4)_3$ (III). The crystal structure of III revealed tetrahedral coordination, with the BH_4 ligands eclipsed by three methyl substituents of the aromatic ring. The cyclopentadienyl complexes $\text{CpU}(\text{BH}_4)_3$, $\text{Cp}_2\text{U}(\text{BH}_4)_2\text{Na}$, $\text{Cp}_3\text{U}(\text{BH}_4)\text{Na}$, and $\text{Cp}_3\text{U}(\text{THF})$ were prepared from II.

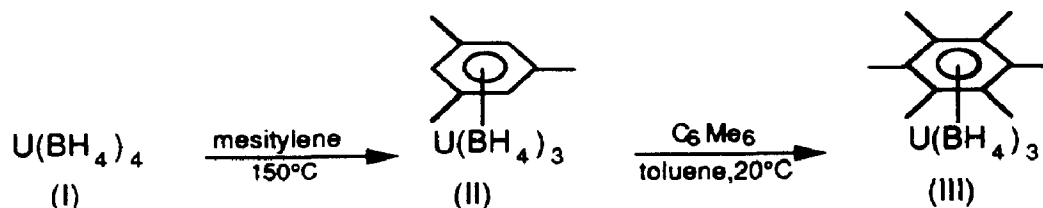
Introduction

The derivatives of the uranium(III) trisborohydride $\text{U}(\text{BH}_4)_3$ [1] are limited to a few adducts with hetero-atom ligands (O,N,P) [2–5], and none of them has been used for the synthesis of organouranium complexes. We have found that the reduction of $\text{U}(\text{BH}_4)_4$ (I) in mesitylene (1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$) affords the arene compound $(\eta\text{-mesitylene})\text{U}(\text{BH}_4)_3$ (II); after displacement of the aromatic ligand, the hexamethylbenzene derivative $(\text{C}_6\text{Me}_6)\text{U}(\text{BH}_4)_3$ (III) is obtained [6]. We report here the synthesis of these rare examples of arene uranium compounds [7–9] and the X-ray crystal structure of III. We also describe some reactions of II which indicate its potential utility in organouranium synthesis.

Results and discussion

Synthesis

The reduction of the uranium(IV) tetraborohydrides to the corresponding $\text{U}(\text{BH}_4)_3$ derivatives [2–5] reflects the ready accessibility of the uranium(III) oxydation state, and the isolation of the phosphine complexes $\text{U}(\text{BH}_4)_3\text{L}_2$ ($\text{L} = \text{PEt}_3$ [3], $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ [4]) showed that soft ligands could be coordinated to the



Scheme 1

$\text{U(BH}_4)_3$ fragment. The arene complex $(\eta\text{-mesitylene})\text{U(BH}_4)_3$ (II) was simply prepared by heating (150°C , 20 min) a suspension of $\text{U(BH}_4)_4$ (I) in the aromatic hydrocarbon; it was isolated as air-sensitive bright red crystals in 80% yield (Scheme 1).

The ^1H NMR spectrum of II in toluene exhibited a large resonance at 150 ppm corresponding to the borohydride ligands, and two pairs of signals which were assigned to the free (7.18 and 2.29 ppm) and coordinated (-12.11 and -18.41 ppm) mesitylene molecules. The latter were in rapid exchange, as demonstrated by spin saturation transfer experiments [10], and the proportion of free mesitylene was less at low temperature (90% at 30°C ; 60% at -50°C). These facts were easily explained in terms of reversible dissociation of the mesitylene ligand, in competition with the aromatic solvent; this dissociation was less important in benzene (65% at 30°C). These results suggested that it should be possible to prepare the arene compound $(\eta\text{-C}_6\text{H}_5\text{Me})\text{U(BH}_4)_3$ by heating a solution of I in toluene. In fact, this thermal decomposition gave a complex mixture of at least 4 uranium borohydrides (see Experimental), but the NMR spectra showed that the expected toluene derivative was the major component of this mixture [11*].

The labile mesitylene ligand of II was readily displaced by hexamethylbenzene to give the complex $(\text{C}_6\text{Me}_6)\text{U(BH}_4)_3$ (III), which did not undergo arene exchange with benzene. This order of stability or decreasing ease of displacement series of the aromatic ligand, $\text{C}_6\text{Me}_6 > \text{C}_6\text{H}_3\text{Me}_3 > \text{C}_6\text{H}_5\text{Me} > \text{C}_6\text{H}_6$, is identical to that invariably observed with the arene *d*-transition metal complexes [12]. Arene derivatives of the *f*-block elements are limited to $(\text{C}_6\text{Me}_6)\text{M(AlCl}_4)_3$ ($\text{M} = \text{Sm, U}$) [7], $(\text{C}_6\text{H}_6)\text{U(AlCl}_4)_3$ [8], and three examples of polynuclear hexamethylbenzene-uranium compounds containing Cl and/or AlCl_4 ligands [9]; all these products were prepared from SmCl_3 or UCl_4 under reductive Friedel-Crafts conditions.

Like the other known arene actinide complexes, II and III were found to be thermally resistant, but in solution were stable only in aromatic solvents. In dichloromethane, they progressively decomposed, presumably by oxidation, into unidentified U^{IV} products; in tetrahydrofuran (THF), they were immediately transformed into $\text{U(BH}_4)_3(\text{THF})_n$, and their recrystallisation from THF/pentane gave $\text{U(BH}_4)_3(\text{THF})_3$ [5]. Addition of 2 equivalents of DMPE (DMPE = $\text{Me}_2\text{PCH}_2\text{CH}_2\text{-PMe}_2$) to a toluene solution of II gave $\text{U(BH}_4)_3(\text{DMPE})_2$ [4].

Well-defined precursors of organouranium compounds in the +3 oxidation state are scarce, and some initial studies showed that the mesitylene complex II should be a useful starting material for them. The reaction with cyclopentadiene in benzene

* Reference marked with an asterisk indicates a note occurring in the list of references.

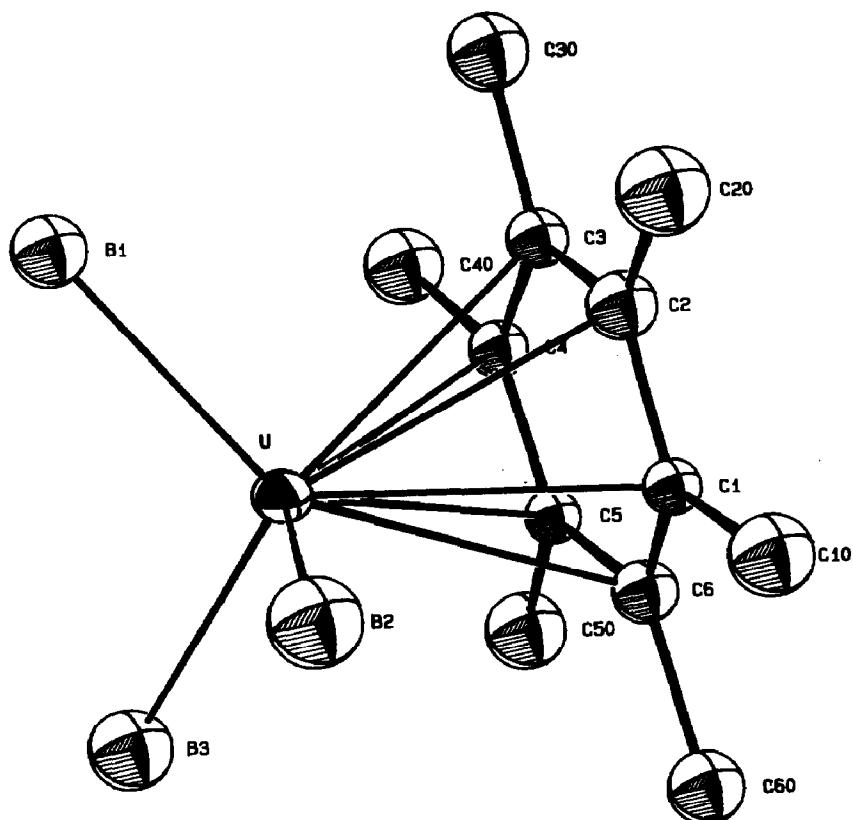


Fig. 1. View of molecule III.

Table 1

Selected bond distances (Å) and angles (°)

U-C(1)	2.87(2)	C(1)-C(2)	1.41(2)
U-C(2)	2.89(2)	C(2)-C(3)	1.41(3)
U-C(3)	2.95(2)	C(3)-C(4)	1.42(3)
U-C(4)	2.95(2)	C(4)-C(5)	1.33(3)
U-C(5)	2.97(2)	C(5)-C(6)	1.44(2)
U-C(6)	2.96(2)	C(6)-C(1)	1.35(3)
U-B(1)	2.54(3)	C(1)-C(10)	1.57(2)
U-B(2)	2.49(4)	C(2)-C(20)	1.51(4)
U-B(3)	2.69(3)	C(3)-C(30)	1.49(3)
		C(4)-C(40)	1.52(3)
		C(5)-C(50)	1.56(3)
		C(6)-C(60)	1.57(1)
B(1)-U-B(2)	112(1)	C(2)-C(1)-C(6)	122(2)
B(1)-U-B(3)	104(1)	C(1)-C(2)-C(3)	118(2)
B(2)-U-B(3)	104(1)	C(2)-C(3)-C(4)	120(2)
		C(3)-C(4)-C(5)	120(2)
		C(4)-C(5)-C(6)	121(2)
		C(5)-C(6)-C(1)	118(1)

gave the monocyclopentadienyl compound $\text{CpU}(\text{BH}_4)_3$ ($\text{Cp} = \eta\text{-C}_5\text{H}_5$) [13], whereas treatment with 2 or 3 equivalents of CpNa gave the uranium(III) anions $\text{Cp}_2\text{U}(\text{BH}_4)_2^-$ [14] and $\text{Cp}_3\text{U}(\text{BH}_4)^-$ [15], respectively. When treated with 3 equivalents of CpK , II was transformed into $\text{Cp}_3\text{U}(\text{THF})$ [16]. The similar formation of pentadienyluranium derivatives is described in the adjacent paper [14].

X-Ray crystal structure of $(\text{C}_6\text{Me}_6)\text{U}(\text{BH}_4)_3$

ORTEP [17] drawings of III are shown in Figs. 1 and 2; selected bond distances and angles are listed in Table 1. The structure consists of discrete neutral molecules of $(\text{C}_6\text{Me}_6)\text{U}(\text{BH}_4)_3$. The arene and borohydride ligands form a distorted tetrahedron around the uranium atom. The planar hexamethylbenzene molecule is parallel to the plane of the three boron atoms. The U–B distances are characteristic of tridentate BH_4 ligands. The U–C bond lengths, which are relatively large and average 2.93 Å, are identical to those in other arene uranium compounds [7–9]. It is noteworthy that the BH_4 ligands of III are eclipsed with respect to three carbon atoms of the arene ring (and three methyl substituents). This preference over the staggered conformation, which must be electronic in origin, was previously observed for other (arene) ML_3 complexes such as (mesitylene) $\text{Mo}(\text{CO})_3$ [18] and $(\text{C}_6\text{Et}_6)\text{M}(\text{CO})_3$ ($\text{M} = \text{Co}, \text{Cr}$) [19] but is, to our knowledge, unprecedented for the hexamethylbenzene derivatives.

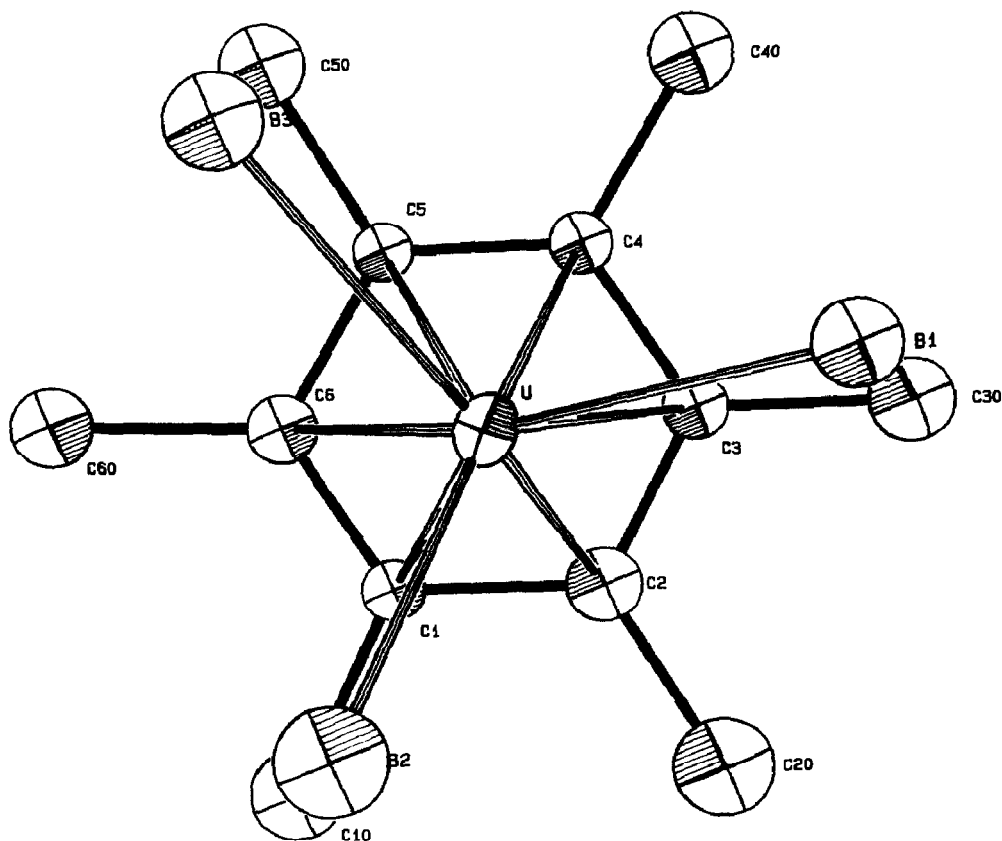


Fig. 2. View of molecule III along perpendicular axis of the C_6Me_6 plane.

Experimental

General methods

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (FRG). The infrared spectra were recorded on a Perkin-Elmer 782 instrument and the ^1H NMR spectra on a Bruker W60 (FT) instrument. Deuteriated solvents were dried over Na/K alloy. The paramagnetic shifts were determined relative to tetramethylsilane ($\delta = 0$); positive values denote shifts to low field.

All experiments were carried out under argon in Schlenk type glassware interfaced to a high vacuum line or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately prior to use. $\text{U}(\text{BH}_4)_4$ was prepared according as described previously [20].

Syntheses

(Mesitylene)U(BH₄)₃ (II). A suspension of I (500 mg) in mesitylene (5 ml) was heated under reflux for 20 min then cooled to 50 °C. The bright red crystals of II were filtered off and dried under vacuum (550 mg, 80%). NMR δ (toluene-*d*₈, 30 °C): 150 (br, 480, 12H, BH₄); 7.18 and 2.29 (s, intensities in the ratio 1/3, free C₉H₁₂); -12.11 and -18.41 (s, intensities in the ratio 1/3, coordinated C₉H₁₂). The total intensity of the signals corresponding to the mesitylene molecule was equal to 12H. The signals of free and coordinated mesitylene were in the ratio 90/10 at 30 °C and 60/40 at -50 °C; this ratio was 65/35 in benzene at 30 °C. Irradiation of the signal at -18.41 ppm caused a decrease in intensity of the signal at 2.29 ppm to 10% of its original value. IR (Nujol): 2486, 2198 and 2128 cm⁻¹. Analysis: Found: C, 26.58; H, 5.74; B, 7.85. C₉H₂₄B₃U calc.: C, 26.84; H, 6.00; B, 8.05%.

(C₆Me₆)U(BH₄)₃ (III). A 50 ml round bottom flask was charged with II (164 mg) and C₆Me₆ (69 mg) and toluene was condensed into the flask under vacuum at -78 °C. The mixture was stirred for 15 min at 20 °C. The solution was filtered and evaporated, to give microcrystals of III, which were washed with pentane (10 ml) and dried under vacuum (160 mg, 90%). NMR δ (benzene-*d*₆, 30 °C): 150 (br, 530, 12H, BH₄); -13.90 (s, 18H, CH₃). IR (Nujol): 2493, 2199, 2122 cm⁻¹. Analysis: Found: C, 32.11; H, 6.99; B, 7.03. C₁₂H₃₀B₃U calc.: C, 32.40; H, 6.80; B, 7.29%.

U(BH₄)₃(Me₂PCH₂CH₂PMe₂)₂. An NMR tube was charged with II (10 mg) and DMPE (7.5 mg) and toluene-*d*₈ was condensed into it. The NMR spectrum revealed quantitative formation of $\text{U}(\text{BH}_4)_3(\text{DMPE})_2$ [4]. NMR δ (toluene-*d*₈, 30 °C): 115 (br, 480, 12H, BH₄); 0.59 (s, 24H, CH₃); -1.24 (s, 8H, CH₂).

U(BH₄)₃(THF)₃. Pentane (10 ml) was added to a solution of II (90 mg) in THF (5 ml). Orange microcrystals were formed within 15 min and were filtered off and dried under vacuum (65 mg, 58%) NMR δ (benzene-*d*₆, 30 °C): 123 (br, 300, 12H, BH₄); 4.68 (br, 25, 12H, THF); 2.73 (br, 20, 12H, THF). IR spectrum and X-ray powder diagram showed that these crystals were identical to those described previously [5].

The NMR spectra of II, III and $\text{U}(\text{BH}_4)_3(\text{THF})_3$ in THF-*d*₈ exhibited a broad quartet (J 73 Hz) at -83.07 ppm corresponding to $\text{U}(\text{BH}_4)_3(\text{THF})_n$.

Thermal decomposition of $\text{U}(\text{BH}_4)_4$ in toluene

A suspension of I (300 mg) in toluene (10 ml) was kept at 130 °C for 15 min. It was then cooled to 50 °C and a red precipitate in a red solution was observed. The

solution was filtered and evaporated. The red precipitate (20 mg), presumably $U(BH_4)_3$ [1], was insoluble in toluene; its NMR spectrum in THF- d_8 exhibited a single resonance corresponding to $U(BH_4)_3(THF)_n$. The red microcrystals (250 mg), which were obtained by evaporation of the solvent, were almost completely soluble in toluene; the NMR spectrum in benzene- d_6 showed signals which were tentatively assigned to (toluene) $U(BH_4)_3$. NMR δ (benzene- d_6 , 30 °C): 150(br, 1000, 12H, BH_4); 6.99(s, 5H, CH); 2.02 (s, 3H, CH_3). A further borohydride signal was also visible at 140 ppm; the peaks at 150 and 140 ppm had intensities in the ratio 90/10. The NMR spectrum of the crystals in THF- d_8 exhibited resonances corresponding to $U(BH_4)_3(THF)_n$ and free toluene. Other less important ($\approx 10\%$) borohydride signals were detected at 230, 214 and 151 ppm; their intensities were found to depend upon the reaction times. Attempts to crystallize (toluene) $U(BH_4)_3$ in toluene led to the formation of increasing quantities of the insoluble red precipitate; the NMR spectrum of the latter in THF- d_8 showed again the signal from $U(BH_4)_3(THF)_n$.

Reaction of II with cyclopentadiene

An NMR tube was charged with II (10 mg); toluene- d_8 (0.5 ml) and CpH (1.5 equiv.) were condensed at $-78^\circ C$ under vacuum. After 3 days at 20 °C, $CpU(BH_4)_3$ [13] was formed in 80% yield (by NMR).

Reaction of II with CpNa and CpK

(a) An NMR tube was charged with II (10 mg) and CpNa (6.5 mg) and THF- d_8 was condensed into it. The NMR spectrum after 15 min showed quantitative formation of the $Cp_3U(BH_4)^-$ anion [15].

(b) A 50 ml round bottom flask was charged with II (100 mg) and CpK (172 mg) and THF (15 ml) was condensed into it under vacuum at $-78^\circ C$. The mixture was stirred for 10 h at 20 °C then filtered and the solution was evaporated to leave red crystals (100 mg, 80%) of $Cp_3U(THF)$, characterized by its NMR spectrum in toluene- d_8 [16].

X-ray analysis

Single crystals of III were obtained in an NMR tube by reducing I (7 mg) in toluene- d_8 (0.5 ml) by Na/Hg (2%, 5 mg) in the presence of C_6Me_6 (4.5 mg); after 20 h, red well shaped crystals were formed. A selected crystal was introduced into a thin-walled Lindeman capillary in an inert atmosphere drybox and data were collected on an Enraf-Nonius CAD4 automatic diffractometer. The lattice parameters were obtained from a least-squares refinement of the setting angles of 25 reflections ($8^\circ \leq \theta \leq 12^\circ$). Intensities were corrected for Lorentz-polarization effects and absorption (Ψ scans [21] and DIFABS [22]). The structure was solved by the heavy-atom method and refined by full matrix least-squares (F). The methyl H atoms were introduced at idealized positions and constrained to ride on their C atoms. H atoms of the BH_4 groups were not located. The absolute structure was determined. The difficulty in solving this structure was to go out of the centrosymmetry; it was necessary to fix the z coordinates of C(1), C(6), C(10) and C(60) in order to avoid collapse. The solution in $P2_1$ space group is a nearly eclipsed projection (B(1)/C(3), B(2)/C(1) and B(3)/C(5)) obtained by the possible inverse rotations (ca. 15°) of the carbon hexagon and the boron triangle. All calculations

Table 2

Crystallographic data and experimental details

<i>Crystal data</i>	
Cryst. dimensions (mm)	0.35 × 0.35 × 0.25
Color	red
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	7.395(7)
b (Å)	14.242(7)
c (Å)	8.725(5)
β (°)	107.22(5)
V (Å ³)	878(2)
Z	2
D_{calc} (g cm ⁻³)	1.683
μ (Mo- K_{α}) (cm ⁻¹)	87.46
<i>Data collection</i>	
Radiation	Mo- K_{α} (λ 0.71073 Å)
θ limits (°)	1-25
Scan type	$\omega/2\theta$
Monochromator	graphite
Reflections measured	
h	-8,8
k	0,16
l	0,10
Reflections collected:	
total	1715
unique	1609
with $I > 3\sigma(I)$	942
Temperature (K)	294
Final values	
$R(F)$	0.042
$R_w(F^2)^a$	0.040

$$^a w = 1/(\sigma F_0)^2 \text{ and } \sigma F_0^2 = [(\sigma I)^2 + (pF^2)^2]^{1/2}; p = 0.04.$$

Table 3

Fractional atomic coordinates, equivalent or isotropic thermal parameters and their e.s.d. for compound III

Atom	x	y	z	$B(\text{Å}^2)$
U	-0.13317(8)	0.899	-0.20634(8)	3.43(1) ^b
C(1)	0.180(2)	0.848(1)	-0.320 ^a	2.7(3)
C(2)	0.230(3)	0.811(2)	-0.163(3)	4.7(5)
C(3)	0.272(2)	0.875(1)	-0.034(2)	3.2(4)
C(4)	0.254(2)	0.972(1)	-0.064(2)	3.4(4)
C(5)	0.211(2)	1.005(1)	-0.214(2)	3.2(4)
C(6)	0.175(3)	0.942(1)	-0.349 ^a	4.5(4)
C(10)	0.150(3)	0.776(2)	-0.461 ^a	6.2(6)
C(20)	0.247(4)	0.706(2)	-0.132(3)	8.1(8)
C(30)	0.331(3)	0.838(2)	0.133(3)	6.5(6)
C(40)	0.297(3)	1.036(2)	0.082(3)	6.0(6)
C(50)	0.214(3)	1.113(2)	-0.240(3)	6.1(6)
C(60)	0.131(3)	0.985(2)	-0.521 ^a	6.0(6)
B(1)	-0.189(4)	0.870(2)	0.063(3)	5.5(7)
B(2)	-0.318(5)	0.789(3)	-0.415(5)	9 (1)
B(3)	-0.289(4)	1.068(2)	-0.299(4)	6.6(7)

^a Coordinate not refined in ultimate cycle. ^b $B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \bar{a}_i \bar{a}_j$.

were performed on a Microvax II computer with the Enraf–Nonius Structure Determination Package [23]. Analytical scattering factors for neutral atoms [24] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 2, and final positional parameters are listed in Table 3.

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