2868 *Inorg. Chem.* **1987**, *26*, 2868-2872

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Preparation and Crystal Structures of Complexes of $U(BH_3CH_3)_4$ with 1,2-Dimethoxyethane, *N,N,N′,N′*-Tetramethylethylenediamine, and 1,2-Bis(methylthio)ethane

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Received February 17, 1987

Complexes of $U(BH_3CH_3)_4$ with $CH_3OCH_2CH_2OCH_3$, $(CH_3)_2NCH_2CH_2N(CH_3)_2$, and $CH_3SCH_2CH_2SCH_3$ have been synthesized and their molecular structures determined by single-crystal X-ray diffraction. $U(BH_3CH_3)_4·CH_3OCH_2CH_2OCH_3$ is tetragonal, $P4/n$, with $a = 21.822$ (8) Å, $c = 7.681$ (5) Å, $Z = 8$, $d = 1.61$ g/cm^3, and $R = 0.028$ [$F^2 > 3\sigma(F^2)$]; $U(BH_3CH_3)_4·(CH_3)_2NCH_2CH_2N(CH_3)_2$ is monoclinic, $P2_1/n$, with $a = 10.206$ (4) Å, $b = 15.436$ (6) Å, $c = 12.880$ (5) Å, $\beta = 92.25$ (3)°, $Z = 4$, $d = 1.54$ g/cm^3, and $R = 0.029$ ($F^2 > 3\sigma(F^2)$); $U(BH_3CH_3)_4·CH_3SCH_2CH_2SCH_3$ is triclinic, $P\bar{1}$, with $a = 8.937$ (4) Å, $b = 13.692$ (4) Å, $c = 8.186$ (3) Å, $\alpha = 96.46$ (4)°, $\beta = 97.64$ (4)°, $\gamma = 74.07$ (4)°, $Z = 2$, $d = 1.66$ g/cm^3, and $R = 0.023$ ($F^2 > 2\sigma(F^2)$). With one exception, all BH_3CH_3 groups are coordinated to the uranium atoms by tridentate hydrogen bridges with a U–B bond distance of 2.55 ± 0.02 Å. For the $(CH_3)_2NCH_2CH_2N(CH_3)_2$ complex one B atom is coordinated to the uranium atom through a bidentate hydrogen bridge with a U–B distance of 2.72 (2) Å and a U–B–C angle of 142 (2)°. Uranium is coordinated to the O, N, and S atoms of the respective ligands with U–O, U–N, and U–S average distances of 2.58 ± 0.04, 2.73 ± 0.01, and 3.07 ± 0.04 Å, respectively.

Introduction

Recently the preparation and crystal structures of two bidentate phosphine adducts, $U(BH_3CH_3)_4·$dmpe and $U(BH_3CH_3)_3·2$dmpe (dmpe = 1,2-bis(dimethylphosphino)ethane) have been reported.[2] All of the $BH_3CH_3^-$ groups of $U(BH_3CH_3)_3·2$dmpe are coordinated to the metal through tridentate hydrogen bridges. Surprisingly in the analogous tetrahydroborate complex $U(BH_4)_3·2$dmpe, two of the BH_4^- groups are coordinated to the metal through tridentate hydrogen bridges while the third BH_4^- group is coordinated to the metal through a terminal bidentate hydrogen bridge.[3] In other compounds, such as $U(BH_4)_4$, bidentate BH_4^- groups can bridge two metal atoms.[4] We have shown that in the dimeric complexes $[Th(BH_3CH_3)_4]_2·OEt_2$ and $[Th(BH_3CH_3)_4·THF]_2$, the $BH_3CH_3^-$ group can serve in a bridging capacity[5] similar to the type of bridging observed in the tetrahydroborate complex, $Co_2(BH_4)_2(Ph_2P(CH_2)_4PPh_2)_2·{}^1/_2C_6H_6$.[6] The methyltrihydroborate and tetrahydroborate groups in these complexes engage in a variety of ligation modes. Undoubtedly these variations are related to subtle changes in the steric environment about the metal.

In this paper we report the syntheses, structures, and solution dynamic behavior of three new bidentate base adducts, $U(BH_3CH_3)_4·$dme (dme = dimethoxyethane), $U(BH_3CH_3)_4·$tmed (tmed = *N,N,N′,N′*-tetramethylethylenediamine), and $U(BH_3CH_3)_4·$bmte (btme = 1,2-bis(methylthio)ethane).

Experimental Section

All preparations were carried out under an argon atmosphere. Hexane was dried over CaH_2 and distilled under argon. Toluene was dried over Na and distilled under argon. Diethyl ether was distilled from sodium benzophenone ketyl. The base 1,2-dimethoxyethane (dme) was dried over CaH_2 and distilled from sodium benzophenone ketyl. *N,N,N′,N′*-Tetramethylethylenediamine (tmed) was dried over NaOH and then BaO, and distilled under argon. The base 1,2-bis(methylthio)ethane (bmte) was prepared according to the literature[7] and dried over CaH_2. $U(BH_3CH_3)_4$ was prepared as described previously.[8]

Infrared spectra were recorded on a Perkin-Elmer IR-283 spectrophotometer and calibrated with polystyrene film. Nujol and Fluorolube mulls were prepared in an argon-filled drybox with dry, degassed Nujol and Fluorolube. Nuclear magnetic spectra were recorded on a JEOL FX 90Q 90-MHz FT spectrometer and referenced to tetramethylsilane.

Table I. Infrared Spectroscopic Data (cm^{-1})

compd				
$U(BH_3CH_3)_4·$dme	2950 m	2190 m	2100 s	1300 s
	1230 s	1080 s	1035 s	950 m
	850 s	820 m	720 w	660 m
$U(BH_3CH_3)_4·$tmed	2950 m	2300 m	2210 s	2150 s
	2110 s	2040 m	1880 w	1300 s
	1280 w	1230 s	1125 m	1110 w
	1095 w	1070 m	1035 w	1010 m
	1000 m	960 w	945 m	915 w
	860 w	790 s	770 m	720 w
	680 w	620 w	595 w	495 w
	475 w	455 w		
$U(BH_3CH_3)_4·$bmte	2950 m	2180 s	2100 s	1430 w
	1410 w	1405 w	1300 s	1260 w
	1235 s	1075 s	1030 m	960 s
	900 w	880 w	840 w	720 w

Table II. ^1H NMR Data for $U(BH_3CH_3)_4·$dme[a,b]

T, °C	BH_3	CH_3	dme
−78	−102.25 (6 H, s)	−31.20 (6 H, s)	−56.52 (4 H, s)
	(679.5)[c]	94.65 (6 H, s)	−44.46 (6 H, s)
−40	*d*	*e*	−47.64 (4 H, s)
			−38.10 (6 H, s)
−20.5	*d*	25.09 (12 H, s)[f]	−42.66 (4 H, s)
			−34.20 (6 H, s)
25	194.25 (12 H, s)[g]	21.43 (12 H, s)[f]	−33.84 (4 H, s)
			−27.57 (6 H, s)

[a] In toluene-d_8. [b] Shifts in ppm from Me_4Si. Positive sign indicates downfield shift. [c] Estimated δ of other BH_3 peak based on extrapolation from averaged BH_3 peak at 25 °C. [d] BH_3 peak broadened into base line due to rapid exchange of BH_3CH_3 sites. [e] CH_3 peak broadened into base line due to rapid exchange of BH_3CH_3 sites. [f] Averaged CH_3 peak. [g] Averaged BH_3 peak.

Table III. ^1H NMR Data for $U(BH_3CH_3)_4·$tmed[a,b]

T, °C	BH_3	CH_3	tmed
−59	−74.50 (6 H, s)[c]	−22.83 (6 H, s)	−40.50 (12 H, s)
		81.11 (6 H, s)	−28.05 (4 H, s)
25	*d*	*e*	−29.64 (12 H, s)
			−16.74 (4 H, s)
54	*f*	19.39 (12 H, s)[g]	−26.40 (12 H, s)
			−14.57 (4 H, s)

[a] In toluene-d_8. [b] Shifts in ppm from Me_4Si. Positive sign indicates downfield shift. [c] Other BH_3 peak not found. [d] BH_3 peak broadened into baseline due to rapid exchange of BH_3CH_3 sites. [e] CH_3 peak broadened into baseline due to rapid exchange of BH_3CH_3 sites. [f] Averaged BH_3 peak not found up to 84 °C. [g] Averaged CH_3 peak.

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0020-1669/87/1326-2868$01.50/0

Table IV. ^1H NMR Data for $U(BH_3CH_3)_4 \cdot bmte$[a,b]

T, °C	BH_3	CH_3	bmte
−78	*c*	−69.98 (6 H, s)	−24.54 (4 H, s)
		80.49 (6 H, s)	−9.90 (6 H, s)
−32	*c*	*d*	−17.53 (4 H, s)
			−8.26 (6 H, s)
−22	*c*	21.78 (12 H, s)	−16.64 (4 H, s)
			−7.92 (6 H, s)
15	182.94 (12 H, s)[e]	19.26 (12 H, s)[f]	−13.30 (4 H, s)
			−6.56 (6 H, s)

[a] In toluene-d_8. [b] Shifts in ppm from Me_4Si. Positive sign indicates downfield shift. [c] No BH_3 peak found. [d] CH_3 peak broadened into baseline due to rapid exchange of BH_3CH_3 sites. [e] Averaged BH_3 peak. [f] Averaged CH_3 peak.

Samples were prepared in toluene-d_8 in an argon-filled drybox and sealed under vacuum or capped with serum stoppers. Melting points were determined in sealed argon-filled capillaries. IR data are given in Table I and ^1H NMR data in Tables II–IV. Elemental analyses were conducted by the analytical laboratories of the University of California, Berkeley.

Preparation of $U(BH_3CH_3)_4 \cdot$dme. $U(BH_3CH_3)_4$ (0.25 g, 0.71 mmol) was dissolved in 10 mL of dme. Excess solvent was removed in vacuo to dryness. The residue was sublimed under vacuum at 125 °C, from which 0.17 g (54% yield) of blue-green, finely crystalline $U(BH_3CH_3)_4 \cdot$dme was recovered; mp 141–142 °C dec. To grow crystals suitable for X-ray structure analysis, the sublimate was dissolved in 10 mL of toluene; the solution was filtered, reduced in volume to 3 mL, and cooled to −20 °C overnight. Blue-green crystals were isolated and washed with cold (−78 °C) ether. Anal. Calcd for $C_8H_{34}B_4O_2U$: C, 21.66; H, 7.72. Found: C, 21.60; H, 7.75.

Preparation of $U(BH_3CH_3)_4 \cdot$tmed. To 0.23 g (0.65 mmol) of $U(BH_3CH_3)_4$ dissolved in 15 mL of hexane was added about 0.10 mL (0.65 mmol) of tmed; a yellow-green precipitate formed. The mixture was stirred for several minutes and pumped dry. The residue was dissolved in 10 mL of toluene, and the solution was filtered, reduced in volume to 3 mL, and cooled at −20 °C overnight. Yellow-green crystals were isolated and washed with cold (−78 °C) ether. A yield of 0.12 g (39% yield) of yellow-green $U(BH_3CH_3)_4 \cdot$tmed was recovered; mp 113–115 °C dec. Anal. Calcd for $C_{10}H_{40}B_4N_2U$: C, 25.57; H, 8.58; N, 5.96. Found: C, 25.44; H, 8.67; N, 5.89.

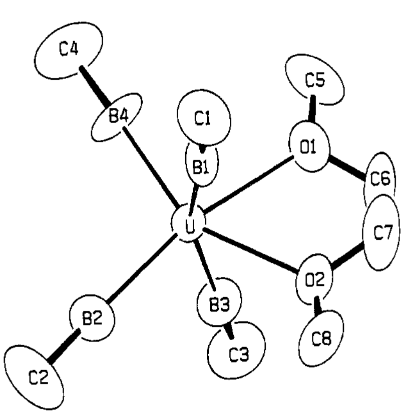

Figure 1. ORTEP drawing of $U(BH_3CH_3)_4 \cdot CH_3OCH_2CH_2OCH_3$.

Preparation of $U(BH_3CH_3)_4 \cdot$bmte. To 0.30 g (0.85 mmol) $U(BH_3CH_3)_4$ dissolved in 15 mL of hexane was added 0.10 mL (0.85 mmol) of bmte with stirring for 10 min, after which the hexane was pumped off. The residue was dissolved in toluene, and the solution was filtered, reduced in volume to 3 mL, and cooled at −20 °C overnight. Deep green crystals were isolated and washed with cold (−78 °C) ether. A yield of 0.23 g (57% yield) of $U(BH_3CH_3)_4 \cdot$bmte was recovered; mp 134–136 °C dec. Anal. Calcd for $C_8H_{34}B_4S_2U$: C, 20.20; H, 7.20; S, 13.48. Found: C, 20.60; H, 7.32; S, 13.39.

X-ray Diffraction. All crystals were sealed inside quartz capillaries to protect them from the atmosphere. The crystals were examined with a Picker automated diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda_{K\alpha}$ = 0.710 73 Å). Cell dimensions and other crystal data are given in Table V. Intensity data were collected

Table V. Summary of Crystal Data, Data Collection, and Least-Squares Results for $U(BH_3CH_3)_4 \cdot L$

	L = $CH_3OCH_2CH_2OCH_3$	L = $(CH_3)_2NCH_2CH_2N(CH_3)_2$	L = $CH_3SCH_2CH_2SCH_3$
cryst syst	tetragonal	monoclinic	triclinic
space group	$P4/n$	$P2_1/n$	$P\bar{1}$
a,[a] Å	21.822 (8)	10.206 (4)	8.937 (4)
b, Å	21.822 (8)	15.436 (6)	13.692 (4)
c, Å	7.681 (5)	12.880 (5)	8.186 (3)
α, deg	90.00	90.00	96.46 (4)
β, deg	90.00	92.25 (3)	97.64 (4)
γ, deg	90.00	90.00	74.07 (4)
V, Å^3	3658	2028	952
T, °C	23	23	23
Z	8	4	2
mol wt	443.63	469.72	475.76
d_{calcd}, g/cm^3	1.61	1.54	1.66
2θ range, deg	$5 < 2\theta < 45$	$4 < 2\theta < 45$	$4 < 2\theta < 47.5$
scan speed	*g*	*g*	*g*
scan range	$1.5 + 0.693 \tan \theta$	$1.5 + 0.693 \tan \theta$	$1.6 + 0.693 \tan \theta$
reflcns measd	$+h,+k,\pm l$	$\pm h,+k,\pm l$	$\pm h,\pm k,\pm l$
no. of reflcns	4863	6836	5830
no. of unique reflcns	2422	2631	2916
cryst size, mm	0.11 × 0.17 × 0.34	0.14 × 0.21 × 0.25	0.08 × 0.08 × 0.16
abs μ, cm^{-1}	84.0	75.8	82.7
abs range	2.33–4.15	2.18–4.22	1.49–2.07
cryst decay cor	1.00–1.08	1.00–1.18	1.00–1.05
extinction factor[b]	1.09×10^{-7}		
no. of data in least squares	1173 ($F^2 > 3\sigma$)	1303 ($F^2 > 3\sigma$)	2270 ($F^2 > 2\sigma$)
p[c]	0.04	0.04	0.03
R; R_w[d]	0.028; 0.031	0.029; 0.030	0.023; 0.025
goodness of fit[e]	1.01	1.02	1.00
max shift/esd[f]	0.05	0.01	0.02
residuals, e/Å^3: min; max	1.63; −1.53	1.60; −1.60	0.85; −0.72

[a] Cell dimensions are based on least-squares fit to the setting angles of several unresolved Mo Kα peaks: for the $CH_3OCH_2CH_2OCH_3$ ligand, 25 reflections, $25° < 2\theta < 36°$; for the $(CH_3)_2NCH_2CH_2N(CH_3)_2$ ligand, 36 reflections, $20° < 2\theta < 32°$; for the $CH_3SCH_2CH_2SCH_3$ ligand, 29 refelections, $19° < 2\theta < 34°$. [b] The empirical extinction correction has the form $F_{cor} = F_{obsd}(1 + kI_{obsd})$, where F is the structure factor, I is the uncorrected intensity, and k is the extinction factor. [c] In the least-squares refinement, the assigned weights to the data are $1.0/[\sigma(F_o)]^2$ were derived from $\sigma(F_o^2) = [S^2 + pF_o^2]$, where S^2 is the variance due to counting statistics and p is assigned a value that adjusts the weights of the stronger reflections to be comparable with the rest of the data. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum(w(\Delta F)^2/\sum(wF_o^2)]^{1/2}$. [e] Goodness of fit = standard deviation of an observation of unit weight = $[\sum w(\Delta F)^2/(n - v)]^{1/2}$, where n = number of reflections and v = number of variables. [f] Non-hydrogen atoms. [g] Variable 2–8° min^{-1} on 2θ.

Table VI. Positional Parameters[a]

atom	*x*	*y*	*z*
	$U(BH_3CH_3)_4{\cdot}CH_3OCH_2CH_2OCH_3$		
U	0.20528 (2)	0.50255 (2)	0.97455 (5)
O(1)	0.1448 (5)	0.5561 (5)	1.2227 (13)
O(2)	0.1725 (5)	0.4344 (6)	1.2281 (13)
B(1)	0.0996 (8)	0.4681 (8)	0.8655 (20)
B(2)	0.2604 (9)	0.4277 (9)	0.7726 (2)
B(3)	0.3000 (9)	0.5165 (8)	1.1726 (25)
B(4)	0.2067 (10)	0.6060 (8)	0.8288 (23)
C(1)	0.0341 (7)	0.4497 (8)	0.7839 (23)
C(2)	0.2934 (8)	0.3808 (9)	0.6498 (25)
C(3)	0.3591 (9)	0.5266 (6)	1.2917 (23)
C(4)	0.2083 (9)	0.6706 (8)	0.7316 (28)
C(5)	0.1338 (9)	0.6208 (9)	1.2441 (26)
C(6)	0.1394 (9)	0.5218 (11)	1.3817 (22)
C(7)	0.1292 (10)	0.4591 (11)	1.3522 (22)
C(8)	0.1743 (9)	0.3710 (9)	1.2257 (22)
	$U(BH_3CH_3)_4{\cdot}(CH_3)_2NCH_2CH_2N(CH_3)_2$		
U	0.18724 (6)	0.23296 (3)	0.33364 (4)
N(1)	0.2330 (13)	0.2027 (8)	0.5402 (8)
N(2)	0.3510 (13)	0.3547 (8)	0.4240 (9)
B(1)	0.2154 (17)	0.3219 (10)	0.1681 (12)
B(2)	0.0286 (21)	0.0933 (13)	0.3006 (16)
B(3)	0.3750 (19)	0.1285 (12)	0.3004 (15)
B(4)	−0.0153 (17)	0.3119 (12)	0.3859 (14)
C(1)	0.2266 (18)	0.3727 (11)	0.0633 (13)
C(2)	−0.1157 (19)	0.0649 (12)	0.3034 (14)
C(3)	0.4927 (18)	0.0650 (11)	0.2829 (16)
C(4)	−0.1375 (21)	0.3646 (15)	0.4226 (17)
C(5)	0.3069 (21)	0.1258 (11)	0.5647 (12)
C(6)	0.1141 (22)	0.1913 (14)	0.5995 (13)
C(7)	0.3031 (23)	0.2793 (15)	0.5837 (12)
C(8)	0.3862 (24)	0.3260 (14)	0.5274 (15)
C(9)	0.2942 (17)	0.4411 (11)	0.4268 (15)
C(10)	0.4762 (18)	0.3632 (10)	0.3744 (14)
	$U(BH_3CH_3)_4{\cdot}CH_3SCH_2CH_2SCH_3$		
U	0.35404 (3)	0.27068 (2)	0.22330 (3)
S(1)	0.11623 (22)	0.36158 (15)	−0.06545 (23)
S(2)	0.34929 (21)	0.10925 (14)	−0.06293 (22)
B(1)	0.1228 (9)	0.2093 (7)	0.2882 (10)
B(2)	0.2813 (10)	0.4503 (6)	0.3637 (10)
B(3)	0.5498 (10)	0.1601 (7)	0.4264 (10)
B(4)	0.5646 (11)	0.2902 (8)	0.0537 (11)
C(1)	−0.0141 (10)	0.1657 (7)	0.3298 (11)
C(2)	0.2429 (10)	0.5617 (6)	0.4554 (11)
C(3)	0.6692 (10)	0.0875 (7)	0.5506 (11)
C(4)	0.6909 (13)	0.3061 (9)	−0.0526 (13)
C(5)	0.1906 (12)	0.4327 (7)	−0.1841 (12)
C(6)	0.2579 (9)	0.1792 (6)	−0.2386 (8)
C(7)	0.1034 (9)	0.2559 (6)	−0.2140 (9)
C(8)	0.2170 (9)	0.0328 (6)	−0.0511 (10)

[a] Here and in subsequent tables the number in parentheses is the estimated standard deviation in the least significant digit.

by using a θ–2θ scan technique. Three standard reflections were measured at every 250th scan, and the intensities were adjusted for the variations in the standards. Lorentz–polarization and absorption corrections (analytical integration method)[9] were made. The structures were refined by a full-matrix least-squares procedure in which the function $\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2$ was minimized. Atomic scattering factors for all atoms except hydrogen were taken from ref 10; the hydrogen scattering factors were those of Stewart, Davidson, and Simpson.[11] Anomalous scattering corrections were used.[12] Three dimensional Patterson maps were used to find the uranium atoms, and subsequent least-squares refinements and electron density maps were used to find the remaining atoms; many of the hydrogen atoms were observed in the maps, and from these the positions of other hydrogen atoms were estimated. Non-hydrogen atoms were assigned anisotropic thermal parameters; hydrogen atoms were included with isotropic thermal parameters, most of which were fixed, and with distance restraints.[13] *R* factors and other statistical results of the least-squares refinements are given in Table V. Local unpublished crystallographic computer programs were used. Positional parameters are given in Table VI, and distances and angles are given in Tables VII and VIII. Tables of thermal parameters, hydrogen positions and restraints, and observed structure factors are given as supplementary material.

Table VII. Selected Distances (Å) in $U(BH_3CH_3)_4{\cdot}L$

L = $CH_3OCH_2CH_2OCH_3$		L = $(CH_3)_2NCH_2$-$CH_2N(CH_3)_2$		L = $CH_3SCH_2CH_2SCH_3$	
U–O(1)	2.60 (1)	U–N(1)	2.72 (1)	U–S(1)	3.09 (1)
U–O(2)	2.55 (1)	U–N(2)	2.74 (1)	U–S(2)	3.04 (1)
U–B(1)	2.57 (2)	U–B(1)	2.56 (2)	U–B(1)	2.57 (1)
U–B(2)	2.55 (2)	U–B(2)	2.72 (2)	U–B(2)	2.55 (1)
U–B(3)	2.58 (2)	U–B(3)	2.55 (2)	U–B(3)	2.54 (1)
U–B(4)	2.52 (2)	U–B(4)	2.51 (2)	U–B(4)	2.57 (1)
O(1)–C(5)	1.44 (2)	N(1)C(5)	1.44 (2)	S(1)–C(5)	1.80 (1)
O(1)–C(6)	1.44 (2)	N(1)–C(6)	1.47 (3)	S(1)–C(7)	1.80 (1)
		N(1)–C(7)	1.48 (3)		
O(2)–C(7)	1.45 (2)	N(2)–C(8)	1.44 (2)	S(2)–C(6)	1.79 (1)
O(2)–C(8)	1.39 (2)	N(2)–C(9)	1.46 (2)	S(2)–C(8)	1.80 (1)
		N(2)–C(10)	1.46 (2)		
B(1)–C(1)	1.61 (2)	B(1)–C(1)	1.57 (2)	B(1)–C(1)	1.59 (1)
B(2)–C(2)	1.57 (3)	B(2)–C(2)	1.54 (3)	B(2)–C(2)	1.59 (1)
B(3)–C(3)	1.60 (3)	B(3)–C(3)	1.58 (3)	B(3)–C(3)	1.59 (1)
B(4)–C(4)	1.60 (3)	B(4)–C(4)	1.58 (3)	B(4)–C(4)	1.59 (1)
C(6)–C(7)	1.40 (3)	C(7)–C(8)	1.35 (3)	C(6)–C(7)	1.51 (1)

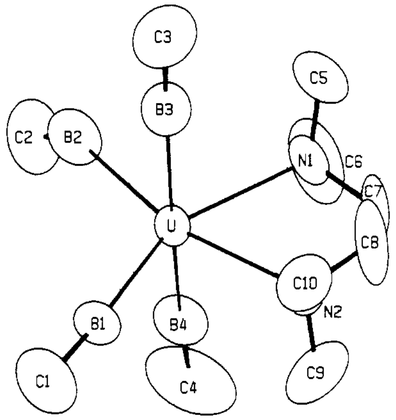

Figure 2. ORTEP drawing of $U(BH_3CH_3)_4{\cdot}(CH_3)_2NCH_2CH_2N(CH_3)_2$.

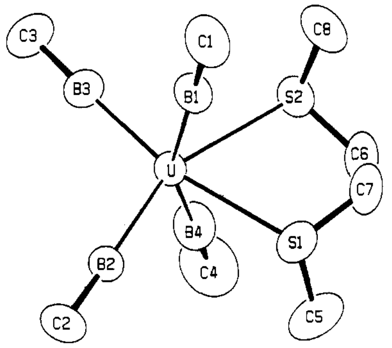

Figure 3. ORTEP drawing of $U(BH_3CH_3)_4{\cdot}CH_3SCH_2CH_2SCH_3$.

Discussion

The uranium atom is at the center of a distorted octahedron; see Figures 1–3. Two boron atoms and two X atoms (X = N, O, or S) are in the equatorial plane with the uranium atom, and the other two boron atoms are above and below the plane.

With one exception, all of the BH_3CH_3 groups are coordinated to the uranium atoms by tridentate hydrogen bridges; the exception is in the (tmed) complex, where the B(2) atom is coordinated to

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Table VIII. Selected Angles (deg) in $U(BH_3CH_3)_4·L$

L = $CH_3OCH_2CH_2OCH_3$		L = $(CH_3)_2NCH_2CH_2N(CH_3)_2$		L = $CH_3SCH_2CH_2SCH_3$	
B(1)–U–B(2)	92.2 (6)	B(2)–U–B(3)	85.3 (6)	B(1)–U–B(3)	93.7 (6)
B(2)–U–B(3)	93. 2(6)	B(2)–U–B(4)	86.4 (7)	B(3)–U–B(4)	94.0 (3)
B(1)–U–B(4)	94.4 (6)	B(1)–U–B(4)	94.7 (6)	B(2)–U–B(4)	98.8 (3)
B(3)–U–B(4)	98.4 (6)	B(1)–U–B(3)	95.2 (6)	B(1)–U–B(2)	99.1 (3)
B(2)–U–B(4)	107.3 (7)	B(1)–U–B(2)	112.3 (6)	B(2)–U–B(3)	107.0 (3)
B(1–)U–B(3)	161.0 (6)	B(3)–U–B(4)	168.9 (7)	B(1)–U–B(4)	157.5 (3)
O(1)–U–O(2)	63.9 (4)	N(1)–U–N(2)	68.0 (4)	S(1)–U–S(2)	69.9 (2)
O(1)–U–B(4)	86.0 (6)	N(2)–U–B(1)	84.2 (5)	S(1)–U–B(2)	85.0 (2)
O(2)–U–B(2)	102.9 (5)	N(1)–U–B(2)	95.5 (5)	S(2)–U–B(3)	98.2 (2)
B(1)–U–X[a]	81.3	B(3)–U–X	90.3	B(1)–U–X	79.7
B(3)–U–X	82.1	B(4)–U–X	89.4	B(4)–U–X	79.7
C(1)–B(1)–U	176 (1)	C(1)–B(1)–U	177 (2)	C(1)–B(1)U	177 (1)
C(2)–B(2)–U	179 (2)	C(2)–B(2)–U	142 (2)	C(2)–B(2)–U	178 (1)
C(3)–B(3)–U	178 (2)	C(3)–B(3)–U	178 (2)	C(3)–B(3)–U	178 (1)
C(4)–B(4)–U	178 (2)	C(4)–B(4)–U	177 (2)	C(4)–B(4)–U	178 (1)

[a] X is the midpoint of atoms O(1)–O–(2), N(1)–N(2), or S(1)–S(2).

Table IX. $\sum$caf Calculations[18] for Uranium Methyltrihydroborate-Base Adducts

compd	coord no.	coord group/atom	dist, Å	caf	$\sum$caf
$U(BH_3CH_3)_4·dme$	14	$U–BH_3$[a]	2.09	0.163	0.812
		U–O	2.58	0.080	
$U(BH_3CH_3)_4·tmed$	13	$U–BH_3$[a]	2.09	0.163	0.799
		$U–BH_2$[b]	2.23	0.073	
		U–N	2.73	0.082	
$U(BH_3CH_3)_4·bmte$	14	$U–BH_3$[a]	2.11	0.160	0.844
		U–S	3.07	0.102	
$U(BH_3CH_3)_4·dmpe$	14	$U–BH_3$[a]	2.15	0.155	0.842
		U–P	3.02	0.111	
$U(BH_3CH_3)_4·tmed$[c]	14[c]	$U–BH_3$[a]	2.09	0.163	0.816
		U–N	2.73	0.082	

[a] The $U–BH_3$ distance is defined as the distance from U to the center of the plane formed by the three bridging H atoms. [b] The $U–BH_2$ distance is defined as the distance from U to the middle of the line connecting the two bridging H atoms. [c] Hypothetical complex with four tridentate methyltrihydroborates.

the U atom through bidentate hydrogen bridges, and the bidentate bridge U–B distance is 2.72 Å with a U–B–C angle of 142°. This bidentate U(IV)–B bond distance may be compared to bridging bidentate U(IV)–B distances found for $U(BH_4)_4$ (2.86 ± 0.03 Å),[14] $U(BH_4)_4·OEt_2$ (2.89 (1) Å),[15a] and $U(BH_4)_4·OMe_2$ (2.89 (2) Å).[15a] It compares favorably with the only known terminal bidentate U(III)–B distance of 2.84 (3) Å,[3] if we assume that the U(III) ionic radius is ~0.13 Å longer than the U(IV) ionic radius.[16]

Bidentate coordination, though common for the tetrahydroborates, has until now not been observed for the methyltrihydroborates. The reason for this unusual bidentate coordination is not due to first-order steric crowding, since the hypothetical $\sum$caf ($\sum$caf = sum of the cone angle factors)[17] for complete tridentate coordination is 0.816, which is even closer to the value of greatest stability (0.8) than that of $U(BH_3CH_3)_4·dmpe$, which has a $\sum$caf value of 0.842 (see Table IX). The anomalous bonding observed for one of the BH_3CH_3 groups in $U(BH_3CH_3)_4·tmed$ could be attributed to either second-order steric crowding caused by the atoms of the coordinating group, which are not themselves directly bonded to the metal, or to crystal packing forces. Second-order crowding is suggested by the U–B(apex)–X angles (where X is the midpoint between the two chelating atoms of the bidentate ligand) (Table VIII). In the tmed complex the U–B(apex) vector is perpendicular to the plane containing U and two nitrogen atoms, whereas in the dme and bmte complexes these vectors are at angles of ~80° to the comparable planes (see Figures 1–3).

The tridentate hydrogen-bridged U–B distances range from 2.51 to 2.57 Å in the three structures with all the U–B–C angles near 180°. For these three complexes the average U–B distance is 2.55 ± 0.02 Å, which compares to 2.48 ± 0.03 Å found in $U(BH_3CH_3)_4$[8] and 2.57 ± 0.02 Å found in $U(BH_3CH_3)_4·dmpe$.[2]

For $U(BH_3CH_3)_4·dme$ the average U(IV)–O bond length, 2.58 (1) Å, is comparable to other U(IV)–O bond lengths found in O-coordinated base adducts of $U(BH_4)_4$ and $U(BH_3CH_3)_4$: 2.44 (1) Å for $U(BH_4)_4·OMe_2$,[15a] 2.485 (5) Å for $U(BH_4)_4·OEt_2$,[15a] 2.48 (4) Å for $U(BH_4)_4·O(n\text{-}Pr)_2$,[15c] 2.47 (1) Å for $U(BH_4)_4·2THF$[15b] and 2.49 (1) Å for $U(BH_3CH_3)_4·2THF$.[18] The average U(IV)–N bond length of 2.73 (1) Å is comparable to other U(IV)–N(neutral) bond lengths: 2.68 (2) Å for both $U\{\eta\text{-}C_5H_4)_2CH_2\}Cl_2·bpy$[19] and $UCp_3NCS·NCMe$.[20] The average U(IV)–S bond length for $U(BH_3CH_3)_4·bmte$ is 3.07 (1) Å. This may be compared to the U(III)–S bond distance of 2.99 (1) Å found for $(MeC_5H_4)_3U·THT$.[21]

Because of the similarities in both steric and electronic properties of the four bidentate bases used to prepare the $U(BH_3CH_3)_4$ base adducts, ligand-exchange studies were performed by ^1H NMR spectroscopy. Toluene-d_8 solutions of one of the bidentate base adducts were equilibrated with 1 or 2 equiv of another bidentate base. Although no K_{eq} values were obtained because of either rapid and complete exchange of one base for another or no exchange at all, a qualitative order of affinity to the metal was determined. The order found was dmpe > tmed > bmte > dme. This order agrees with recent ligand-exchange studies of $(MeC_5H_4)_3U·L$ (L = THF, py, quinuclidine, PMe_3) and $(MeC_5H_4)_3M·L$ (M = Ce, Nd; L = PMe_3, py) in which the softer base PMe_3 has a greater affinity for the metal than the nitrogen- and oxygen-coordinated bases.[21,22]

The solution behavior of the pseudo-six-coordinate $U(BH_3CH_3)_4·L$ (L = dme, tmed, bmte) parallels that of $U(BH_3CH_3)_4·dmpe$.[2] Tables II–IV show the observed chemical shifts for BH_3CH_3 groups. At low temperatures, two CH_3 resonance peaks are observed due to the BH_3CH_3 groups cis and trans to the

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coordinating atoms of the bidentate base. As the temperature is raised, the inequivalent BH_3CH_3 groups exchange rapidly, leading to coalescence of the peaks. For $U(BH_3CH_3)_4$·dme, coalescence of methyl peaks occurs at ~−40 °C; for $U(BH_3CH_3)_4$·tmed, ~25 °C; for $U(BH_3CH_3)_4$·bmte, ~−20 °C, and for $U(BH_3CH_3)_4$·dmpe, ~10 °C.[2] The chemical shift difference between cis and trans CH_3 protons is ~126 ppm at −78 °C for $U(BH_3CH_3)_4$·dme, ~104 ppm at −59 °C for $U(BH_3CH_3)_4$·tmed, ~150 ppm at −78 °C for $U(BH_3CH_3)_4$·bmte, and ~63 ppm at −20 °C for $U(BH_3CH_3)_4$·dmpe.[2] From these data a free energy of activation of ~10 kcal/mol can be obtained for all four complexes. It is not possible to establish a unique mechanism with the present data.

Acknowledgment. This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

Registry No. $U(BH_3CH_3)_4$·dme, 97201-93-9; $U(BH_3CH_3)_4$·tmed, 109391-53-9; $U(BH_3CH_3)_4$·bmte, 97201-96-2.

Supplementary Material Available: Tables S1–S7, listing thermal parameters, distance restraints on hydrogen atoms, and hydrogen positions (7 pages); tables of calculated and observed structure factors (33 pages). Ordering information is given on any current masthead page.

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Ruthenium(III)-Promoted Hydrolysis of Chelated Glycinamide in Acidic Solution

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Received February 19, 1987

(Glycinamide-*N*,*O*)tetraammineruthenium(III) reacts in dilute aqueous acid solution (pH 1–3) to give a mixture of (glycinato)tetraammineruthenium(III) and *cis*-diaquotetraammineruthenium(III). The yields of the products were calculated and compared to yields of NH_4^+. The yields are pH dependent contrary to the rate, which is pH independent: $k = (4.9 \pm 0.4) \times 10^{-5}\ s^{-1}$ (μ = 0.1 M, 23 ± 1 °C). A mechanism that involves a rate-determining nucleophilic attack of a water molecule on the carbonyl of chelated glycinamide is suggested. For the analogous chelates of ethyl glycylglycinate and of *N*′-ethylglycinamide, the rate is at least 2 orders of magnitude slower than that for the glycinamide chelate. This is the first demonstration of a significant promotion of a chelated amino acid amide hydrolysis by a metal ion at room temperature, in a solution of acidic pH.

Introduction

Metal ion promoted hydrolysis of amino acid esters and peptides has been a subject of numerous studies for many years.[1-4] These include studies of activation by labile metal ions such as Cu(II), Zn(II), Ni(II), Cd(II), Hg(II), and Pb(II),[1-3] as well as studies of activation by the inert metal ions Co(III)[4] and Ru(III).[5] Hydrolysis is rendered facile by chelation of the amino acid derivative through the amino nitrogen and the carbonyl oxygen. Attachment of the carbonyl group to the metal ion makes the carbon atom more susceptible toward nucleophilic attack.

The reactivity of the kinetically inert Co(III) complexes of amino acid derivatives has been thoroughly studied by the groups of Buckingham and Sargeson.[4,6] Analogous complexes of another kinetically inert metal ion—Ru(III)—were prepared and studied more recently.[5,7,8] By studying systems that contain inert metal ions rather than labile metal ions, one has the advantage of knowing the structure and properties of the starting reactants and the ability to define more unequivocally intermediates and mechanisms.

Chelation of esters, as well as of amides and peptides of amino acids to Co(III), enhances their hydrolysis under basic conditions. In acidic solutions, hydrolysis of Co(III)-chelated amino acid esters is also enhanced significantly.[4] In contrast, Co(III)-chelated amino acid amides and peptides are stable toward hydrolysis at low pH.[9] Similarly, the effect of other metal centers on the hydrolysis of amino acid amides and peptides in acid solution is small, and elevated temperatures are needed in order to study it.[1-3]

The chemistry of Ru(III) complexes of amino acid derivatives shows significant deviations from the chemistry of the analogous Co(III) complexes.[5,7,8] Thus, contrary to the stability of Co(III)-chelated glycinamide in acidic pH, Ru(III)-chelated glycinamide undergoes parallel hydrolysis and aquation in acid solution.

The results of studies of the reactivity of Ru(III)-chelated glycinamide and its derivatives in the pH range 1–3 are presented here.

Experimental Section

Chemicals and Reagents. Chloropentaammineruthenium(III) chloride was prepared from ruthenium trichloride[10] and was purified by recrystallization from 0.1 M HCl. *cis*-Diaquotetraammineruthenium(III) trifluoromethanesulfonate was prepared from chloropentaammineruthenium(III) chloride as described before.[8a,11]

Glycinamide hydrochloride and ethyl glycylglycinate (Sigma) were used without further purification. *N*′-Ethylglycinamide hydrochloride was prepared as described before.[8a]

CF_3SO_3H (Fluka, purum) was distilled under reduced pressure in an ungreased apparatus and kept in a desiccator at ~4 °C. $CF_3SO_3Na\cdot H_2O$ was prepared by neutralizing CF_3SO_3H with NaOH (~10 M) and drying the resulting product in a vacuum desiccator over NaOH.

All other chemicals were reagent grade and were used as received. Deionized water that was distilled from an all-glass apparatus was used throughout.

Preparation of Complexes. (Glycinamide-*N*,*O*)tetraammineruthenium(II) hexafluorophosphate ($[(NH_3)_4\overline{RuNH_2CH_2CO}NH_2](PF_6)_2$, I) was prepared as described.[8a] Solutions of (ethyl glycylglycinate-*N*,*O*)tetraammineruthenium(III) (II) and of (*N*′-ethylglycinamide-*N*,*O*)tetraammineruthenium(III) (III) were prepared by oxidizing the corresponding ruthenium(II) pentaammine complexes, isolated as the

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