Inorganica Chimica Acta, 95 (1984) 207–209

The Structure of $U_3(O)(OCMe_3)_{10}$, an Unusual Trinuclear U(IV) Oxo-Alkoxide

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Received January 21, 1984

In an attempt to prepare tetrakis(tert-butoxy)-uranium(IV) a trinuclear oxo-alkoxide of uranium-(IV) was obtained instead. The compound has the formula $U_3O[(CH_3)_3CO]_{10}$ and it crystallizes in the hexagonal space group $P6_3mc$ with $a = b = 18.256(4)$ Å, $c = 10.013(2)$ Å, $Z = 2$. The trinuclear unit is strikingly reminiscent of that in $Mo_3O(OCH_2CMe_3)_{10}$. In contrast to the molybdenum compound where there is metal–metal bonding, the U···U distance of 3.574(1) Å indicates a non-bonded interaction.

Introduction

The preparation of uranium(IV) alkoxides has been reported by Gilman and coworkers as early as 1956 [1]. Although the corresponding transition metal alkoxide compounds have revealed a most interesting chemical and structural behaviour [2], including metal–metal bonding, it appears that no effort was made to structurally characterize the uranium(IV) alkoxides.

The method of preparation followed one of the general synthetic routes to metal alkoxides, *viz.*, substitution of the chlorides on an appropriate metal chloride by amides, followed by alcoholysis [3]. In the specific case of $[U^{IV}(OCMe_3)_4]_n$ the reaction was performed in liquid ammonia with KNH_2 prepared *in situ*. The reproducibility of this procedure was later questioned [4]. We have recently learned to prepare a homoleptic U^{IV} t-butoxide, $K\{U_2(OCMe_3)_9]$, in a reproducible way [5]. During early attempts to obtain $[U(OCMe_3)_4]_n$, however, we obtained the title compound, $U_3O(OCMe_3)_{10}$, **1**.

Experimental

Preparation

$U_3O(OCMe_3)_{10}$, **1**, was obtained as pale green prismatic crystals when following, to the best of our knowledge, a literature procedure [1]. The UCl_4 was from a commercial source but it was purified by reported procedures [6]. The procedure differed from later preparations of the homoleptic U^{IV} t-butoxide compound in that the green hexane extract was kept at room temperature for an extended period of time.

X-ray Crystallography

General procedures for both data collection and crystallographic computing [7] were conventional ones. All geometric and intensity data were taken from a crystal mounted in a thin-walled glass capillary using an automated four-circle diffractometer (Syntex P$\bar{1}$), equipped with graphite-monochromated Mo radiation. The lattice vectors were identified by application of the automated indexing routine of the diffractometer to the positions of 15 centered reflections with $10° \leqslant 2\theta \leqslant 21°$. Axial photographs as well as preliminary diffractometer data were employed to determine the Laue class. Based on the systematic absences, the choice of possible space groups was restricted to $P6_3/mmc$, P62c and $P6_3mc$. Absorption corrections were made by an empirical method based on ψ-scans of several reflections occurring near $\chi = 90°$.

The position of the heavy atom was determined from a three-dimensional Patterson map. Refinement in the centrosymmetric space group $P6_3/mmc$ left a residual of $R = 0.11$. This implied that the uranium atom was dominating the structure factors to a degree which would make it difficult to locate and refine the remaining non-hydrogen atoms. A difference Fourier map based on the uranium position indicated that the symmetry operators of the centrosymmetric space group, in particular the mirror plane perpendicular to the three-fold axis, were too restrictive. We thus continued to develop and refine the remainder of the molecule in the non-centrosymmetric space group $P6_3mc$. While the core, including the α-carbon atoms, refined in a satisfactory manner, the difference Fourier map was rather shallow in the region of the methyl groups of the terminal butoxides. We thus included atomic positions for these atoms only if the refinement converged at feasible bond distances and angles. During the last cycles of refinement, none of the correlation coefficients exceeded 0.59. Data

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0020-1693/84/$3.00

pertaining to the data collection and refinement are listed in Table I.

A table of observed and calculated structure factors is available from F.A.C. The atomic positional and thermal vibration parameters are listed in Table II.

TABLE I. Crystallographic Data and Parameters for $U_3O(OCMe_3)_{10}$.

Formula	$C_{40}H_{90}O_{11}U_3$
Formula weight	1461.25
Space group	$P6_3mc$
Systematic absences	$hh\bar{2h}l$ $l = 2n$
a, Å	18.256(4)
b, Å	18.256(4)
c, Å	11.013(2)
α, degrees	90.0
β, degrees	90.0
γ, degrees	120.0
V, Å^3	3179(6)
Z	2
d_{calc}, g/cm^3	1.527
Crystal size, mm	0.3 × 0.3 × 0.15
μ(Mo Kα), cm^{-1}	72.658
Data collection instrument	Syntex P$\bar{1}$
Radiation (monochromated in incident beam)	Mo Kα
Orientation reflections, number, range (2θ)	15, $10° \leqslant 2\theta \leqslant 21°$
Temperature, °C	23 ± 2
Scan method	$\omega - 2\theta$
Data col. range, 2θ, deg.	$4° \leqslant 2\theta \leqslant 52°$
No. unique data, total	984
with $F_o^2 > 3\sigma(F_o^2)$	506
Number of parameters refined	44
Trans. factors, max., min.	0.336, 0.113
R^a	0.049
$R_w{}^b$	0.059
Quality-of-fit indicator^c	1.072
Largest shift/esd, final cycle	0.48
Largest peak, e/Å^3	≤1.0

$^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma(|F_o|^2)$. ^{c}Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

TABLE II. Positional Parameters and Their Estimated Standard Deviations for $U_3O(OCMe_3)_{10}{}^a$.

Atom	x	y	z	B (Å^2)
U	0.26809(4)	0.536	0.250	3.04(3)
O(1)	0.333	0.667	0.163(5)	4(1)*
O(2)	0.333	0.667	0.394(4)	1.8(8)*
O(3)	0.234(1)	0.468	0.084(3)	4.5(7)*
O(4)	0.217(1)	0.435	0.379(3)	6.1(9)*
O(5)	−0.830(1)	−0.415	0.238(3)	2.9(5)*
C(1)	0.333	0.667	0.514(7)	2(1)*
C(2)	0.381(2)	0.619	0.564(4)	4(1)*
C(3)	−0.918(2)	−0.459	0.229(3)	2.3(8)*
C(4)	0.524(2)	0.476	0.617(5)	5(1)*
C(5)	0.055(2)	0.594(3)	0.314(4)	8(1)*
C(6)	0.227(3)	0.454	−0.043(8)	9(2)*
C(7)	0.172(3)	0.345	0.457(7)	10(2)*
C(8)	0.123(3)	0.356(3)	0.541(5)	10(1)*

^{a}Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Results

Crystals of $U_3O(OCMe_3)_{10}$ consist of a regular molecular array with no unusual contacts. A view of one molecule, excluding methyl groups, is shown in Fig. 1 while important bond lengths and angles are listed in Table III. The trinuclear unit is composed of three distorted octahedra sharing an edge while also being mutually confacial, and is required crystallographically to have C_{3v} symmetry. It is strikingly similar to the trimeric molybdenum compound $Mo_3O(OCH_2CMe_3)_{10}$ [8] where there are Mo–Mo single bonds (*ca.* 2.5 Å). The U···U distance is 3.574(1) Å which is indicative of a net repulsive, non-bonded interaction between the metal centers.

We have observed elsewhere that very large U–O–C angles suggest that uranium is a good acceptor for ligand π-electrons [5]. In this compound we again find the U–O–C bond angles of the terminal butoxides to be very large, *viz.*, 158° and 170°.

The formation of the trinuclear unit is difficult to explain mechanistically. We have observed before, however, that the homoleptic U^{IV} t-butoxide under-

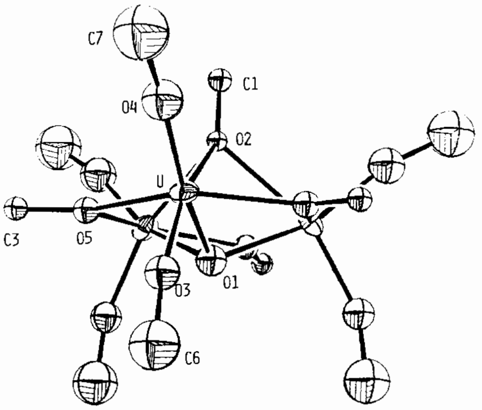

Fig. 1. An ORTEP drawing of the central part of the $U_3O(OCMe_3)_{10}$ molecule. The methyl groups are omitted for clarity.

TABLE III. Principal Internuclear Distances (Å) and Angles (Deg.).

U•••U	3.573(1)
U–O(1)	2.27(3)
U–O(2)	2.61(3)
U–O(3)	2.12(3)
U–O(4)	2.14(3)
U–O(5)	2.373(5)
O(2)–C(1)	1.32(9)
O(3)–C(6)	1.42(9)
O(4)–C(7)	1.60(5)
O(5)–C(3)	1.40(4)
U–U–U	60° (by crystal symmetry)
O(1)–U–O(2)	62(2)
O(1)–U–O(3)	96(2)
O(1)–U–O(4)	163(2)
O(1)–U–O(5)	70.4(4)
O(2)–U–O(3)	158(1)
O(2)–U–O(4)	101(1)
O(2)–U–O(5)	77.2(6)
O(3)–U–O(4)	101(1)
O(3)–U–O(5)	97(1)
O(5)–U–O(5)	141.5(9)
U–O(3)–C(6)	158(1)
U–O(4)–C(7)	170(3)

goes spontaneous oxidation in hexane solution at 5 °C to a mixed oxidation state compound, $U_2(OCMe_3)_9$ [5]. Consistently, Bradley and coworkers reportedly obtained only the quinquevalent alkoxide when following the same literature [1] procedures. It thus seems that the reaction conditions, and in particular the temperature during the workup procedure, strongly influence the nature of the products isolated.

From our point of view, the most interesting result of this work is the observation that even though this $U_3O(OR)_{10}$ molecule is structurally the same, in a qualitative sense, as $Mo_3O(OCH_2Me_3)_{10}$ [8], and the U^{IV} atoms, like Mo^{IV} atoms, have two electrons available for metal–metal bond formation, no U–U bonds are formed. This observation is consistent with our previous findings [5] for other U^{IV} and U^{V} alkoxide compounds, where no U–U bonding occurred, in contrast to the preference of molybdenum and tungsten in their alkoxides to form M–M bonds. Clearly, uranium has much less tendency to M–M bonding, but as we have noted before [5] alkoxides may not be the best possible ligand to foster U–U bond formation because of their tendency to employ metal orbitals as receptor orbitals in the formation of O → U π-bonds.

Acknowledgement

We are grateful to the Robert A. Welch Foundation Grant A-494 for financial support.

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