Synthesis and Solid State Structure of Tetra(2,6-di-isopropylphenoxy)-hexamethoxy-di-tantalum(V), $Ta_2(OC_6H_3Pr^i_2)_4(OCH_3)_6$

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Abstract

The reaction of $Ta(OAr\text{-}2,6\text{-}Pr^i_2)_2(CH_3)_3$(OAr-2,6-$Pr^i_2$ = 2,6-di-isopropylphenoxide) with oxygen in hexane solvent has allowed the isolation of the mixed alkoxide, aryloxide $Ta_2(OAr\text{-}2,6\text{-}Pr^i_2)_4(OCH_3)_6$ (**1**) as large white crystals which have been studied by X-ray diffraction methods. Crystal data for $Ta_2C_{54}H_{86}O_{10}$, $M_r = 1257.16$, monoclinic, $P2_1/a$, $a = 22.137(7)$, $b = 10.494(3)$, $c = 12.452(4)$ Å, $\beta = 105.09(2)°$, $V = 2792(2)$ Å^3, $Z = 2$, $D_x = 1.495$ g cm^{-3}, Mo Kα, $\lambda = 0.71069$ Å, $\mu = 39.2$ cm^{-1}, $F(000) = 636$, $T = 112$ K, $R = 0.030$ for 3212 unique observed reflections. The structure consists of an octahedral arrangement of oxygen donor atoms around two tantalum metal centers in an edge-shared bi-octahedron with two bridging methoxide ligands. The other four methoxide and four phenoxide ligands are terminal.

Introduction

The number of structurally characterized transition metal complexes containing both alkoxide and aryloxide ligands is small [1]. As part of our ongoing studies of the early transition metal chemistry associated with sterically demanding aryloxide ligands we have isolated a mixed alkoxide, phenoxide of tantalum and wish to report here its structure.

Results and Discussion

While investigating the reactivity of the tri-methyl complex $Ta(OAr\text{-}2,6Pr^i_2)_2(CH_3)_3$(OAr-2,6-$Pr^i_2$ = 2,6-di-isopropylphenoxide) [2], the complex was exposed to excess oxygen in hexane solution at 20 °C. The reaction was found to produce a complex mixture of products. However, slow cooling of the hexane mixture yielded a few large crystals of a single product. Structural studies showed the product to be a methoxide dimer **1** formed by insertion of oxygen atoms into the three $Ta–CH_3$ bonds. The clean formation of methoxide groups by insertion of oxygen into $Ti–CH_3$ and $Zr–CH_3$ bonds has been reported by Wolczanski [3], and some insight into the mechanism of these important oxygenations has been obtained.

The molecular structure of **1** is shown in Fig. 1. The crystallographic data is collected in Table I while Table II lists the final atomic positional parameters. Some selected bond distances and angles are given in Table III. The molecule can be seen to adopt an edge-shared bi-octahedral arrangement of oxygen atoms around the two tantalum metal centers. Two methoxide ligands are bridging, while the four aryloxides are terminal, lying in equatorial positions mutually *cis* and *trans* to the bridging methoxides. The four other methoxide ligands occupy the axial terminal positions in the structure, mutually *trans*. A crystallographic inversion center is present. The formation of a dimeric structure of this type is common for homoleptic alkoxides of niobium and tantalum in the +5 oxidation state [4], and the structure of **1** can be related to those reported for $Nb_2(OCH_3)_{10}$ [5] and $Ta_2(OAr\text{-}4Me)_{10}$ [6] (OAr-4Me = 4-methylphenoxide). The distances to the bridging methoxide oxygen atoms are longer by 0.15 Å than the distance to the terminal methoxide oxygen atoms. This difference is comparable to the differences seen in $Ta_2(OAr\text{-}4Me)_{10}$ [6]. The distances to the terminal methoxide and aryloxide ligands are essentially the same, with little noticeable lengthening of the Ta–OAr distance. However, the Ta–O–C angles are on average larger for the terminal phenoxides 160.6(4) and 178.9(4)°, than for the terminal methoxides, 144.8(5) and 167.6(5)°. Large M–O–Ar angles are a characteristic feature of high-valent early transition metal phenoxide chemistry and this effect has been discussed [1]. Both the short ter-

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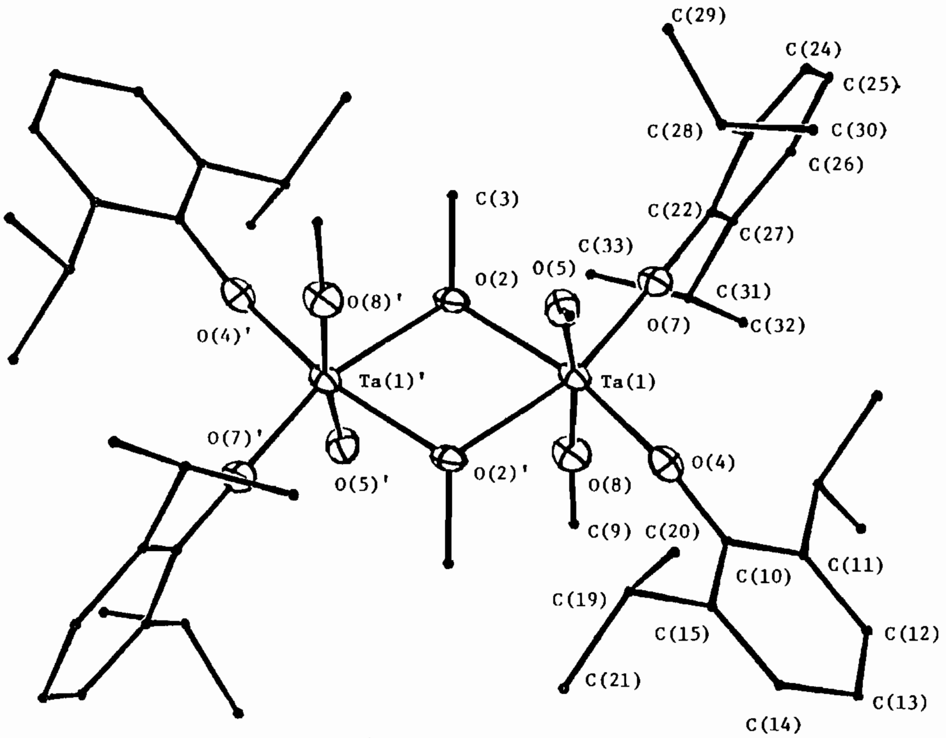

Fig. 1. ORTEP drawing $Ta_2(OAr\text{-}2,6Pr^i_2)_4(OCH_3)_6$ (1). For clarity the thermal ellipsoids of atoms outside of the metal coordination sphere have been reduced.

TABLE I. X-ray Diffraction Data

Formula	$Ta_2O_{10}C_{54}H_{86}$
Formula weight	1257.16
Space group	$P2_1/a$
a (Å)	22.137(7)
b (Å)	10.494(3)
c (Å)	12.452(4)
β (deg)	105.09(2)
Z	2
V (Å^3)	2792.95
D_c (g/cm^3)	1.495
Crystal size (mm)	0.08 × 0.08 × 0.08
Crystal color	colorless
Radiation	Mo Kα (λ = 0.71069 Å)
Linear absorption coefficient (cm^{-1})	39.188
T (°C)	−161
Detector aperture	3.0 mm wide × 4.0 mm high 22.5 cm from crystal
Sample to source distance	23.5 cm
Takeoff angle (deg)	2.0
Scan speed (deg/min)	6.0
Scan width (deg)	2.0 + 0.692 tan θ
Background counts (s)	6
2θ range (deg)	6–45
Data collected	4662
Unique data	3676
Unique data with $F_o > 2.33\sigma(F)$	3212
$R(F)$	0.030
$R_w(F)$	0.032
Goodness of fit	0.817
Largest Δ/σ	0.05

TABLE II. Fractional Atomic Coordinates (×10^4) and Thermal Parameters (Å^2 × 10)

Atom	x	y	z	B_{iso}
Ta(1)	9482.7(1)	231.7(2)	8736.2(2)	14
O(2)	10252(2)	−905(4)	9609(3)	16
C(3)	10242(3)	−2262(6)	9414(6)	21
O(4)	8842(2)	1469(4)	8383(3)	16
O(5)	10099(2)	1359(4)	8460(3)	19
C(6)	10570(4)	1508(8)	7898(8)	43
O(7)	9440(2)	−561(4)	7330(3)	19
O(8)	8970(2)	−1051(4)	9113(4)	20
C(9)	8648(4)	−2146(8)	9234(8)	40
C(10)	8384(3)	2386(6)	8138(5)	18
C(11)	8517(3)	3549(6)	7682(5)	21
C(12)	8036(4)	4431(7)	7419(6)	27
C(13)	7460(4)	4211(8)	7580(6)	33
C(14)	7346(3)	3065(7)	8045(6)	28
C(15)	7802(3)	2118(6)	8342(5)	20
C(16)	9155(3)	3822(7)	7501(6)	27

(continued)

TABLE II. *(continued)*

Atom	*x*	*y*	*z*	B_{iso}
C(17)	9467(5)	4972(10)	8142(9)	55
C(18)	9113(5)	4019(12)	6297(8)	63
C(19)	7708(3)	883(7)	8897(6)	25
C(20)	7021(4)	453(8)	8651(7)	38
C(21)	7989(4)	965(8)	10137(7)	35
C(22)	9289(3)	−1403(6)	6467(5)	18
C(23)	9773(3)	−1991(6)	6131(6)	22
C(24)	9597(4)	−2812(7)	5210(7)	31
C(25)	8981(4)	−2998(8)	4654(7)	34
C(26)	8515(3)	−2415(7)	5027(7)	31
C(27)	8649(3)	−1610(6)	5937(6)	21
C(28)	10461(3)	−1732(7)	6655(6)	24
C(29)	10744(3)	−930(8)	5889(7)	34
C(30)	10844(4)	−2966(9)	6990(7)	37
C(31)	8141(3)	−913(7)	6301(6)	23
C(32)	8040(4)	415(7)	5754(6)	28
C(33)	7531(4)	−1644(9)	6096(7)	38

minal Ta–O distances and large Ta–O–C angles are consistent with the presence of some oxygen-p to metal-d π-bonding in these electron deficient metal complexes [7].

Experimental

The trimethyl complex $Ta(OAr\text{-}2,6Pr^i_2)_2(CH_3)_3$ was synthesized by previously reported methods. A colorless, saturated solution in hexane was exposed to an atmopshere of di-oxygen on a calibrated gas manifold at room temperature. The resulting pale yellow solution was cooled slowly to −15 °C to yield a few large crystals of the methoxide **1** suitable for X-ray diffraction study.

A nearly equidimensional (0.08 × 0.08 × 0.08 mm) sample was cleaved from a larger crystal and handled using standard inert atmosphere techniques [8, 9] and transfered to the goniostat of a modified Picker automatic diffractometer. Cell dimensions were obtained from 36 reflections at −161 °C. The structure was solved by a combination of direct methods and Fourier techniques. All hydrogen atoms were located and refined isotropically.

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TABLE III. Selected Bond Distances (Å) and Angles (°)

Distances	
Ta(1)–O(2)	2.112(4)
Ta(1)′–O(2)	2.131(4)
Ta(1)–O(4)	1.888(4)
Ta(1)–O(5)	1.903(4)
Ta(1)–O(7)	1.919(4)
Ta(1)–O(8)	1.897(4)
Angles	
O(2)–Ta(1)–O(2)′	73.0(2)
O(2)–Ta(1)–O(4)	162.9(2)
O(2)–Ta(1)–O(5)	85.6(2)
O(2)–Ta(1)–O(7)	93.8(2)
O(2)–Ta(1)–O(8)	85.8(2)
O(4)–Ta(1)–O(5)	93.4(2)
O(4)–Ta(1)–O(7)	103.3(2)
O(4)–Ta(1)–O(8)	94.8(2)
O(5)–Ta(1)–O(7)	88.4(2)
O(5)–Ta(1)–O(8)	171.5(2)
O(7)–Ta(1)–O(8)	91.6(2)
Ta(1)–O(2)–Ta(1)′	107.0(2)
Ta(1)–O(2)–C(3)	118.8(4)
Ta(1)–O(4)–C(10)	178.9(4)
Ta(1)–O(5)–C(6)	144.8(5)
Ta(1)–O(7)–C(22)	160.6(4)
Ta(1)–O(8)–C(9)	167.6(5)

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