Polyhedron Vol. 6, No. 9, pp. 1765–1774, 1987
Printed in Great Britain

0277–5387/87 \$3.00+.00

STERICALLY CONGESTED *TRIS* PHENOXIDE COMPLEXES OF TANTALUM(V). THE X-RAY CRYSTAL STRUCTURES OF $[TaCl_2$(2,6-DI-t-BUTYLPHENOXIDE)$_3]$ AND $[Ta_2Cl(\mu\text{-}Cl)_2$(2,6-DI-ISOPROPYLPHENOXIDE)$_5(\mu\text{-}O)]$

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(*Received* 8 *December* 1986; *accepted* 25 *March* 1987)

Abstract—$TaCl_5$ reacts with two equivalents of lithium 2,6-di-t-butylphenoxide in benzene to give $[TaCl_3$(2,6-di-t-butylphenoxide)$_2]$ (**1**) in 70% yield and with three equivalents of the lithium phenoxide in diethyl ether to give $[TaCl_2$(2,6-di-t-butylphenoxide)$_3]$ (**2**) which can also be prepared by reaction of (**1**) with one equivalent of the lithium phenoxide. Three equivalents of lithium 2,6-di-isopropylphenoxide react with $TaCl_5$ to give $[TaCl_2$(diethylether)(2,6-di-isopropylphenoxide)$_3]$ (**4**) which, on attempted recrystallization in the presence of air, gave $[Ta_2Cl(\mu\text{-}Cl)_2$(2,6-di-isopropylphenoxide)$_5(\mu\text{-}O)]$ (**5**). Complexes (**1**), (**2**), and (**4**) were characterized by elemental analysis, IR, and ^1H and ^{13}C NMR spectra. Coordination of the phenoxide ligand in (**2**) is accompanied by downfield shifts of the phenyl ring *ipso*, *ortho* and *para* carbon resonances of 9.6, 3.6 and 3.1 ppm respectively, compared with the free ligand. For complex (**4**) the relative shifts are 5.9, 6.1 and 2.9 ppm. The structures of (**2**) and (**5**) have been determined by single-crystal X-ray diffraction methods. Crystals of (**2**) are monoclinic, space group $P2_1/c$ with $a = 18.902(6)$ Å, $b = 10.815(8)$ Å, $c = 20.259(4)$ Å and $\beta = 92.62(2)°$; crystals of (**5**) are monoclinic, space group $P2_1/c$ with $a = 11.174(1)$ Å, $b = 20.402(4)$ Å, $c = 27.143(3)$ Å and $\beta = 94.58(1)°$. Both structures were solved by Patterson and Fourier methods and refined to R values of 0.063 for the 1690 observed data for (**2**) and 0.062 for the 3693 observed data for (**5**). Complex (**2**) is monomeric with a square pyramidal coordination geometry about Ta. Observed distances are: $Ta\text{–}O_{axial}$ 1.83(2) Å; $Ta\text{–}O_{basal}$ each 1.90(2) Å; $Ta\text{–}Cl_{basal}$ each 1.37(1) Å. Complex (**5**) is binuclear with a distorted octahedral geometry about each tantalum atom. The structure consists essentially of $TaCl_2$(2,6-di-isopropylphenoxide)$_3$ and $TaCl_2$(O)(2,6-di-isopropylphenoxide)$_2$ units bridged through the oxygen and Cl atoms. Observed distances are $Ta\text{–}O_{bridge}$ 1.69(1) and 2.10(1) Å; $Ta\text{–}Cl_{bridge}$ 2.498(7), 2.396(8), 2.634(7) and 2.781(7) Å; $Ta\text{–}Cl_{terminal}$ 2.309(8) Å. The $Ta\text{–}O_{phenoxide}$ distances range from 1.77(2) to 2.19(2) Å. In both (**2**) and (**5**) the phenyl rings are orientated such as to minimise interactions between the 2- and 6-substituents. In both molecules electron counts are maximized using π-electron density from the terminal ligands.

There are now many examples of early transition metal complexes which contain the phenoxide ligand (-OPh).[1,2] Recent interest has centred on complexes containing alkyl substituents at the 2,6 positions of the phenoxide phenyl ring, as unusual coordination geometries and coordinatively unsaturated molecules can result.[3–10] In general, the structures of complexes containing bulky ligands cannot be rationalised on steric grounds alone, as there is always a subtle interplay of both steric and electronic factors.[11,12] However, where a series of related complexes can be prepared in which the steric size of a particular ligand is able to be varied structural changes may be related more specifically to steric effects.

For tantalum(V), a variety of phenoxide complexes have been synthesised. The pentaphenoxide

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[Ta(OPh)$_5$], and the mixed chloro-phenoxides [$TaCl_{5-x}(OPh)_x$] have been prepared from $TaCl_5$ and phenol.[13,14] Reactions between a series of lithium 2,6-disubstituted phenoxides and $TaCl_5$ have given the *penta* phenoxide complex using lithium 2,6-dimethylphenoxide, the *tris* phenoxide complex using lithium 2-t-butyl-6-methylphenoxide and *bis*-phenoxide complexes using lithium 2,6-diisopropylphenoxide and lithium 2,6-di-t-butylphenoxides.[15] Of the complexes prepared, only [$TaCl_3$(2,6-di-t-butylphenoxide)$_2$] has been characterised by X-ray crystallography.[15]

As part of our studies of the chemistry of group V transition metals we have prepared complexes containing three sterically demanding phenoxide ligands. We report here the preparation and characterisation of *tris* 2,6-di-isopropylphenoxide and *tris* 2,6-di-t-butylphenoxide complexes of tantalum(V) and the X-ray crystal structures of [$TaCl_2$(2,6-di-t-butylphenoxide)$_3$] and [$Ta_2Cl(\mu\text{-}Cl)_2$(2,6-di-isopropylphenoxide)$_5(\mu\text{-}O)$].

RESULTS AND DISCUSSION

2,6-*Di-t-butylphenoxide complexes*

It has previously been reported that tantalum pentachloride reacts with an excess of lithium 2,6-di-t-butylphenoxide in benzene to give the *bis* phenoxy complex [$TaCl_3$(2,6-di-t-butylphenoxide)$_2$] (**1**) in 30–40% yield.[15] We have found however that the complex can be obtained in an improved yield of up to 71% if two equivalents of the lithium phenoxide are employed.

The ^{13}C NMR spectrum of (**1**) shows that on coordination of the phenoxide the *ipso* carbon signal shifts downfield by 9.9 ppm compared with the free ligand, the *ortho* and *para* carbon resonances each shift by 5.5 ppm, while the *meta* carbon resonance shifts by 1.1 ppm.

Deshielding of these carbons indicates electron withdrawal from the aromatic ring.[16] The methyl carbons of the t-butyl group show a single resonance, shifted 2 ppm downfield from the free ligand, while the quaternary carbon resonance position is unchanged.

When tantalum pentachloride was reacted with slightly more than three equivalents of lithium 2,6-di-t-butylphenoxide in diethyl ether for up to 24 h, an orange coloured solution formed from which the *bis* phenoxy complex (**1**) could again be obtained. However, when the reaction was carried out for longer periods, the solution colour paled to yellow. After a total reaction period of 3 days, isolation of the product gave a gummy material containing the *tris* phenoxy complex [$TaCl_2$(2,6-di-t-butylphenoxide)$_3$] (**2**). This complex could also be obtained by reacting the *bis* phenoxy complex (**1**) with slightly more than one equivalent of the lithium phenoxide reagent.

The gummy *tris* phenoxide product obtained from these reactions failed to solidify and we have been unable to crystallise the product directly from hydrocarbon solvents in which it is very soluble. However it is only slightly soluble in acetonitrile, addition of which causes the complex to precipitate out analytically pure, in a yield of approximately 40%. Further complex can be obtained from the washings, bringing the total yield to *ca*. 50%. The success of this procedure results from the complex being suitably non-polar whereas the lithium phenoxide reagent, the phenol and the *bis* phenoxy complex (**1**) are all sufficiently polar to dissolve in acetonitrile.

Pure [$TaCl_2$(2,6-di-t-butylphenoxide)$_3$] (**2**) decomposes slowly in air but more rapidly in solution. It is soluble in hydrocarbon solvents and is best crystallised from benzene solution from which large yellow crystals are obtained. In the infrared spectrum the OH absorption of the free ligand is absent, and in the 1300–1000 cm^{-1} region where ν(C–O)Ta is characteristically observed[17] there are two strong absorptions at 1160 and 1088 cm^{-1}. In addition, the spectrum contains absorbances at 880, 875, 690, 463 and 320 cm^{-1} which are not present in the free ligand. The bands at 463 and 320 cm^{-1} are assigned to Ta–O and Ta–Cl vibrations respectively on the basis of tentative assignments made for similar bands in the *bis*-phenoxy complex (**1**).[15]

The ^1H NMR spectrum of (**2**) (Table 1) shows only one resonance for the methyl protons of the t-butyl group, no phenol OH proton resonance and an aromatic multiplet similar to that found for the free ligand. In the ^{13}C NMR spectrum only one set of resonances for the three phenoxide ligands is observed. The *ipso* carbon resonance is shifted downfield 9.6 ppm compared with the free ligand while the *ortho*, *para* and *meta* carbon resonances show downfield shifts of 3.6, 3.1 and 1.3 ppm respectively. The *ortho* and *para* carbon shifts are smaller than those observed for the *bis* phenoxide complex (**1**) which suggests slightly less electron withdrawal from the aromatic rings when three phenoxide ligands are present. This feature may be related to the overall π-bonding properties of the ligands (see later).

Crystal structure of [$TaCl_2$(2,6-di-t-butylphenoxide)$_3$] (**2**)

A crystal structure determination of [$TaCl_2$(2,6-di-t-butylphenoxide)$_3$] (**2**) was carried out to com-

Table 1. NMR spectra[a]

Complex	^1H NMR[b]		^{13}C NMR[b,c]				
	substituent	aromatics	substituent	*ipso*	*ortho*	*meta*	*para*
2,6-di-t-butylphenol	1.45(s,18H,6Me) 5.19(s,1H,OH)	6.64–7.0(m,1H,H_{para}) 7.05–7.35(m,2H,H_{meta})	30.3(Me_3) 34.3(C)	153.8	135.8	124.8	119.6
[$TaCl_3$(2,6-di-t-butylphenoxide)$_2$] (**1**)	1.34(s,36H,12Me)	6.66–7.0(m,2H,H_{para}) 7.00–7.35(m,4H,H_{meta})	32.9(Me_3) 35.8(C)	163.6 (+9.9)	141.3 (+5.5)	125.9 (+1.1)	125.1 (+5.5)
[$TaCl_2$(2,6-di-t-butylphenoxide)$_3$] (**2**)	1.36(s,54H,18Me)	6.63–7.0(m,3H,H_{para}) 7.02–7.40(m,6H,H_{meta})	33.1(Me_3) 36.3(C)	163.4 (+9.6)	139.4 (+3.6)	126.1 (+1.3)	122.7 (+3.1)
2,6-di-isopropylphenol	1.23(d,12H,4Me) 3.15(sep,2H,2CH) 4.90(b,1H,OH)	6.82–7.31(m,3H,$H_{meta,para}$)	22.7(Me_2) 27.0(CH)	149.8	133.6	123.3	120.5
[$TaCl_2$(diethylether)(2,6-di-isopropylphenoxide)$_3$] (**4**)[d]	1.10(d,36H,12H) 3.78(bsep,6H,6CH)	6.70–7.20(m,9H,$H_{meta,para}$)	25.4(Me_2) 25.9(CH)	155.7 (+5.9)	139.7 (+6.1)	123.4 (+0.1)	123.4 (+2.9)

[a] Spectra obtained in dry $CDCl_3$, values in ppm downfield from internal TMS.

[b] Assignments in parentheses, b = broad, d = doublet, m = multiplet, s = singlet, sep = septet.

[c] Figures in parentheses show downfield shift (+ve values) compared with free ligand.

[d] Diethyl ether resonances: ^1H NMR, 1.24 (triplet, 6H, 2Me), 3.45–4.20 (obscured quartet, 4H, $2CH_2$); ^{13}C NMR, 12.7 (CH_3), 66.6 (CH_2).

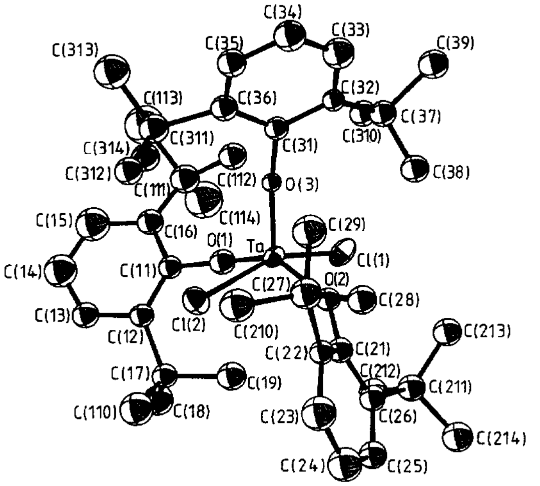

Fig. 1. Molecular geometry and atomic numbering for $[TaCl_2(2,6\text{-di-t-butylphenoxide})_3]$ (**2**).

pare its geometry with those of the *bis* phenoxy complexes $[TaCl_3(2,6\text{-di-t-butylphenoxide})_2]$ (**1**)[15] and $[Ta(Me)_3(2,6\text{-di-t-butylphenoxide})_2]$ (**3**).[18] The molecular structure of (**2**) is shown in Fig. 1 and bond lengths and angles are contained in Table 2. The molecule adopts a square pyramidal geometry about the tantalum atom with one 2,6-di-t-butylphenoxide ligand occupying the axial position and the other two occupying opposite sites of the square pyramid base. The two chloro ligands fill the remaining basal positions. The geometry is thus similar to that observed for the *bis* phenoxy complex (**1**) but it differs from the trigonal bipyramidal geometry of $[Ta(Me)_3(2,6\text{-di-t-butylphenoxide})_2]$ (**3**).[18]

The axial Ta–O bond length (1.83(2) Å) is considerably shorter than the two basal Ta–O bond lengths (each 1.90(2) Å), as was found in the *bis* phenoxy complex (**2**) (Table 3 compares data for complexes (**1**) and (**2**).) The axial Ta–O–C bond angle 162(2)° is larger than the two basal Ta–O–C bond angles (153(2)° and 148(2)°). All these angles are significantly smaller than those observed for the *bis* phenoxy complex (**1**). The two Ta–Cl bond lengths are slightly longer than the equivalent bond lengths in $[TaCl_3(2,6\text{-di-t-butylphenoxide})_2]$ (**1**) but lie within the range found for other tantalum(V) complexes.

Several features relating to π-bonding arise from the molecular dimensions observed. The Ta–O and Ta–Cl bond distances are all shorter than expected for single bonds and this is apparently a consequence of the low formal electron count for the molecule. If the chloro and phenoxide ligands are regarded formally as one-electron donors for purposes of the 18-electron rule then the molecule has an electron count of 10. Adoption of the square-pyramidal geometry increases the ability for ligand to metal π-bonding,[18] thus increasing the formal electron count. In general, -OR ligands are better π-donors than are chloro ligands.[19] In complex (**2**), where three phenoxides are capable of donating π-electron density to the metal, the Ta–Cl bonds are slightly longer than those in the *bis* phenoxy complex (**1**) (see Table 3). An 18-electron count can theoretically be attained if three phenoxides and just one of the chloro ligands act as 3-electron donors, with the remaining chloride acting as a 1-electron donor. However, the structure shows that all of the Ta–O and Ta–Cl bonds are relatively short, indicating that all are involved in π-bonding to the metal. The Ta–O(3) bond (1.83(2) Å) is sufficiently short to suggest that the axial phenoxide acts as a full 3-electron donor with the basal ligands sharing the remaining contribution

Table 2. Selected bond lengths and angles for $[TaCl_2(2,6\text{-di-t-butylphenoxide})_3]$ (**2**)

	(a) Bond lengths (Å)		
Ta—Cl(1)	2.37(1)	Ta—O(3)	1.83(2)
Ta—Cl(2)	2.37(1)	O(1)—C(11)	1.38(4)
Ta—O(1)	1.90(2)	O(2)—C(21)	1.42(4)
Ta—O(2)	1.90(2)	O(3)—C(31)	1.47(4)
	(b) Bond angles (°)		
Cl(1)—Ta—Cl(2)	156.4(4)	O(1)—Ta—O(2)	145.3(8)
Cl(1)—Ta—O(1)	84.9(7)	O(1)—Ta—O(3)	106.2(8)
Cl(1)—Ta—O(2)	89.7(6)	O(2)—Ta—O(3)	108.4(8)
Cl(1)—Ta—O(3)	102.9(6)	Ta—O(1)—C(11)	153(2)
Cl(2)—Ta—O(1)	86.0(7)	Ta—O(2)—C(21)	148(2)
Cl(2)—Ta—O(2)	85.6(6)	Ta—O(3)—C(31)	162(2)
Cl(2)—Ta—O(3)	100.5(7)		

Table 3. Comparison of selected structural data for [TaCl$_3$(2,6-di-t-butylphenoxide)$_2$] (1)[a] and [TaCl$_2$(2,6-di-t-butylphenoxide)$_3$] (2)[b]

(1)		(2)		
		(a) Bond distances (Å)		
Ta—Cl(2)	2.339(2)	Ta—Cl(1)	2.37(1)	
Ta—Cl(3)	2.358(2)	—		
Ta—Cl(4)	2.335(2)	Ta—Cl(2)	2.37(1)	
Ta—O(20)	1.836(4)	Ta—O(3)	1.83(2)	
Ta—O(5)	1.872(5)	Ta—O(1)	1.90(2)	
—		Ta—O(2)	1.90(2)	
		(b) Bond angles (°)[c]		
Cl(2)—Ta—Cl(4)	143.8(1)	Cl(1)—Ta—Cl(2)	156.4(4)	[+12.6]
Cl(3)—Ta—O(5)	155.8(1)	O(2)—Ta—O(1)	145.3(8)	[−10.5]
O(5)—Ta—O(20)	104.2(2)	O(1)—Ta—O(3)	106.2(8)	[+2.0]
Cl(3)—Ta—O(20)	100.0(1)	O(2)—Ta—O(3)	108.4(8)	[+8.4]
Cl(2)—Ta—O(20)	105.8(1)	Cl(1)—Ta—O(3)	102.9(6)	[−2.9]
Cl(4)—Ta—O(20)	110.1(1)	Cl(2)—Ta—O(3)	100.5(7)	[−9.6]
Cl(2)—Ta—O(5)	87.5(1)	Cl(1)—Ta—O(1)	84.9(7)	[−2.6]
Cl(2)—Ta—Cl(3)	84.0(1)	Cl(1)—Ta—O(2)	89.7(6)	[+5.7]
Cl(3)—Ta—Cl(4)	85.1(1)	Cl(2)—Ta—O(2)	85.6(6)	[+0.5]
Cl(4)—Ta—O(5)	88.6(1)	Cl(2)—Ta—O(1)	86.0(7)	[−2.6]

[a] Data taken from Reference 15.

[b] Data from present work.

[c] Values in square parentheses show change in bond angles (2) compared with those of (1). Positive values indicate angle opens, negative values angle closes relative to [TaCl$_3$(2,6-di-t-butylphenoxide)$_2$] (1).

to the π-bonding through a series of PhO⇄Ta and Cl⇄Ta canonicals. The basal Ta–O–C bond angles are smaller in complex (**2**) compared with (**1**) but the bond lengths are not sufficiently different to confirm less π-donation from the phenoxide oxygens in (**2**).

While the overall geometries of the *bis* and *tris* phenoxy complexes are similar, it is of interest to examine the effect of adding the third bulky phenoxide ligand. Bond angles for the two complexes are compared in Table 3. The O(1)–Ta–O(3) bond angle in (**2**) is similar to the equivalent bond angle in (**1**). In both molecules the t-butyl groups of the axial phenoxide are positioned over the basal chlorine ligands while the plane of the two phenyl rings is approximately perpendicular (for (**2**) the angle made by the two planes is 115(1)°). Addition of the third phenoxide ligand opens up the Cl–Ta–Cl bond angle by 12.6° and decreases the equivalent Cl(2)–Ta–O(3) bond angle by 9.6° while the O(2)–Ta–O(3) bond angle (equivalent to the Cl(3)–Ta–O(20) bond angle in (**1**)) opens up by 8.4° resulting in a decrease of the equivalent O(1)–Ta–O(2) bond angle by 10.5°. Changes in the other bond angles are comparatively small.

The phenyl rings in complex (**2**) are positioned to minimise steric interactions between t-butyl substituents. The aromatic ring of the third phenoxide lies somewhat below the basal plane at an angle of 57° to the plane made by the axial phenoxide phenyl ring. As observed in the *bis* phenoxy complex the t-butyl group attached to C(12) in (**2**) occupies the "open" site *trans* to the axial Ta–O bond. We have been unable to refine the positions of the hydrogens on the methyl groups but a non-bonded metal–proton interaction similar to that found in (**1**)[15] is likely to be present. However the ^1H NMR spectrum indicates that in solution all protons are equivalent.

2,6-*Di-isopropylphenoxide complexes*

Tantalum pentachloride reacts with three equivalents of lithium 2,6-di-isopropylphenoxide in diethyl ether to give a yellow-orange coloured solution which pales considerably when the reaction period is extended to 20–36 h. The product isolated persisted as a yellow gum and we have so far been unable to obtain reliable analytical data. However, on the basis of the chlorine analysis and spectroscopic data, the product was characterised as [$TaCl_2$(diethylether)(2,6-di-isopropylphenoxide)$_3$] (**4**). The complex is very soluble in hydrocarbons and in polar solvents such as MeCN or $MeNO_2$, but resisted crystallisation from these media.

The infrared spectrum does not contain OH absorptions and there are bands at 1262 and 1200 cm^{-1} characteristic of ν(C–O)M.[1] In the far infrared the Ta–Cl stretch occurs at 295 cm^{-1}. In the ^1H NMR spectrum the methyl protons of the isopropyl group appear as a slightly broadened doublet, the methine proton as a broadened septet shifted 0.6 ppm downfield compared with the free ligand and the spectrum does not contain an OH proton resonance. In addition, the spectrum contains a quartet and a triplet which integrate as one diethyl ether molecule for every three phenoxide ligands. In the ^{13}C NMR spectrum there is only one set of phenoxide resonances. The *ipso* carbon resonance shows a downfield shift of 5.9 ppm compared with the free ligand, while the *ortho*, *para* and *meta* carbon resonances show downfield shifts of 6.1, 2.9 and 0.1 ppm respectively. The methyl and methine carbons of the isopropyl groups show small downfield shifts of 1.7 and 1.1 ppm.

During attempts to crystallise [$TaCl_2$(diethylether)(2,6-di-isopropylphenoxide)$_3$] (**4**) from petroleum ether, air was inadvertently admitted into the crystallisation flask. After several weeks a small quantity of yellow crystals was obtained, which are identified as [$Ta_2Cl(\mu\text{-}Cl)_2$(2,6-di-isopropylphenoxide)$_5(\mu\text{-}O)$] (**5**) by X-ray crystallography.

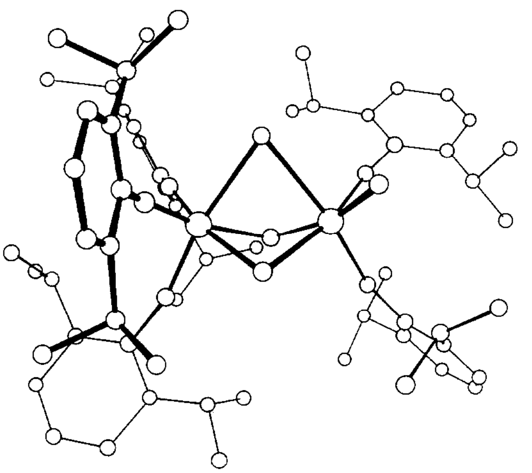

Fig. 2. Molecular geometry for [$Ta_2Cl(\mu\text{-}Cl)_2$(2,6-di-isopropylphenoxide)$_5(\mu\text{-}O)$] (**5**).

Crystal structure of [$Ta_2Cl(\mu\text{-}Cl)_2$(2,6-di-isopropylphenoxide)$_5(\mu\text{-}O)$] (**5**)

The crystal structure determination shows the complex to be binuclear (Figs 2 and 3) in which the two tantalum atoms are in distorted octahedral geometries and are bridged by oxo and two chloro ligands. The oxo ligand lies *trans* to a chloro ligand on one tantalum atom and *trans* to a 2,6-di-isopropylphenoxide ligand on the other. Both bridging chlorides lie *trans* to phenoxide ligands. Bond distances and angles for the molecule are contained in Table 4.

The short Ta(1)–O(1) bond distance (1.69(1) Å) and long Ta(2)–O(1) bond distance (2.10(1) Å) indicate an asymmetric bridge in which oxygen forms a double bond to Ta(1) and a 2-electron sigma bond to Ta(2). The two Ta–Cl–Ta bridges are also asymmetric, the Ta–Cl bond lengths indicating that both Cl(1) and Cl(3) form essentially single bonds to Ta(1). The Ta(1)–Cl(3) bond length at 2.781(7) Å is extremely long and probably represents the limit of lone pair donation from chlorine to a tantalum(V) centre. By comparison, in [$TaCl_2(\mu\text{-}Cl)(NPh)(SMe_2)]_2$ the Ta–Cl bond length *trans* to the phenylimido ligand (which exerts a strong *trans*

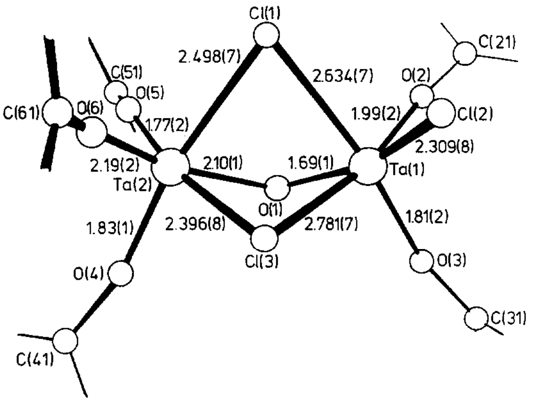

Fig. 3. Inner coordination geometry for [$Ta_2Cl(\mu\text{-}Cl)_2$(2,6-di-isopropylphenoxide)$_5(\mu\text{-}O)$] (**5**).

Table 4. Selected bond lengths and angles for [$Ta_2Cl(\mu\text{-}Cl)_2(2,6\text{-di-isopropylphenoxide})_5(\mu\text{-}O)$] (**5**)

	(a) Bond lengths (Å)		
Ta(1)—Cl(1)	2.634(7)	Ta(2)—Cl(1)	2.498(7)
Ta(1)—Cl(2)	2.309(8)	Ta(2)—Cl(3)	2.396(8)
Ta(1)—Cl(3)	2.781(7)	Ta(2)—O(1)	2.10(1)
Ta(1)—O(1)	1.69(1)	Ta(2)—O(4)	1.83(1)
Ta(1)—O(2)	1.99(2)	Ta(2)—O(5)	1.77(2)
Ta(1)—O(3)	1.81(2)	Ta(2)—O(6)	2.19(2)
O(2)—C(21)	1.50(3)	O(4)—C(41)	1.29(2)
O(3)—C(31)	1.41(2)	O(5)—C(51)	1.32(3)
		O(6)—C(61)	1.58(6)
	(b) Bond angles (°)		
Cl(1)—Ta(1)—O(1)	83.3(5)	Cl(1)—Ta(2)—O(1)	79.5(5)
Cl(1)—Ta(1)—Cl(3)	73.1(2)	Cl(1)—Ta(2)—Cl(3)	82.5(2)
Cl(1)—Ta(1)—Cl(2)	73.2(3)	Cl(1)—Ta(2)—O(5)	86.5(5)
Cl(1)—Ta(1)—O(2)	95.4(5)	Cl(1)—Ta(2)—O(6)	85.6(4)
Cl(1)—Ta(1)—O(3)	170.1(5)	Cl(1)—Ta(2)—O(4)	168.7(5)
Cl(2)—Ta(1)—Cl(3)	74.4(2)	Cl(3)—Ta(2)—O(6)	78.7(5)
Cl(2)—Ta(1)—O(1)	150.0(5)	O(1)—Ta(2)—O(6)	158.5(6)
Cl(2)—Ta(1)—O(2)	103.0(5)	O(5)—Ta(2)—O(6)	110.0(6)
Cl(2)—Ta(1)—O(3)	107.3(5)	O(4)—Ta(2)—O(5)	101.8(7)
Cl(3)—Ta(1)—O(1)	81.1(5)	Cl(3)—Ta(2)—O(1)	84.1(5)
Cl(3)—Ta(1)—O(2)	168.6(5)	Cl(3)—Ta(2)—O(5)	165.5(5)
Cl(3)—Ta(1)—O(3)	97.4(5)	Cl(3)—Ta(2)—O(4)	88.0(5)
O(1)—Ta(1)—O(2)	97.5(7)	O(1)—Ta(2)—O(5)	84.6(6)
O(1)—Ta(1)—O(3)	92.7(7)	O(1)—Ta(2)—O(4)	93.5(6)
O(2)—Ta(1)—O(3)	94.0(6)	O(4)—Ta(2)—O(6)	98.6(6)
Ta(1)—Cl(1)—Ta(2)	71.5(2)	Ta(1)—Cl(3)—Ta(2)	70.4(3)
Ta(1)—O(1)—Ta(2)	104.4(7)	Ta(2)—O(5)—C(51)	158.7(13)
Ta(1)—O(2)—C(21)	174.5(14)	Ta(2)—O(6)—C(61)	161.5(12)
Ta(1)—O(3)—C(31)	162.8(12)	Ta(2)—O(4)—C(41)	161.9(13)

influence) is shorter at 2.751(3) Å.[20] The two Ta–Cl–Ta bond angles in the phenoxide dimer are 70.4(2) and 71.5(2)° which are considerably smaller than those observed in [$TaCl_2(\mu\text{-}Cl)(NPh)(SMe_2)$]$_2$ (103.6°).[20] The Cl–Ta–O(1) bond angles are similar on both sides of the dimer, while the Cl(1)–Ta(1)–Cl(3) bond angle is 11° smaller than the Cl(1)–Ta(2)–Cl(3) bond angle.

For the 2,6-di-isopropylphenoxide ligands, the Ta-O bond lengths range from 1.77(2) to 2.19(2) Å, a wider range than that found in the *tris* 2,6-di-t-butylphenoxide complex (**2**) (1.83(2) to 1.90(2) Å). The ligands about each tantalum atom are considerably distorted from ideal octahedral geometry (see Table 4) as a result of the two halves of the molecule being chemically distinct. For example, the O(2)–Ta(1)–O(3) angle is 94.0(6)° whereas the three O–Ta(2)–O bond angles average 103.5°; Cl(1)–Ta–Cl(3) is 73.1(2)° whereas Cl(1)–Ta(2)–Cl(3) is 82.5(2)°.

The Ta–O–C bond angles range from 161(1)° to 174(2)° and on average are larger than the Ta–O–C bond angles observed for the *tris* 2,6-di-t-butylphenoxide ligands in complex (**2**). At Ta(1) the angles are such as to push the phenyl rings away from the bridge structure. At Ta(2) the Ta–O–C angles are such that the equatorial phenoxides bend away from each other while the axial phenoxide ligand bends into the space between them. In this way the isopropyl substituents at the 2,6-positions of the phenyl rings are able to minimise steric repulsions.

All the phenyl rings orientate on either side of the molecule so as to minimise interactions between the isopropyl groups (see Fig. 3). The isopropyl groups themselves are rotated so that all the methyl groups project away from the metal centres. A corollary is the methine hydrogens in each case project towards the metal centres. However none of these hydrogens make particularly close approaches to Ta, Cl or O atoms.

The structural features thus show that the molecule is able to maintain a +5 oxidation state for each tantalum atom as it consists essentially of TaCl(phenoxide)$_2$(O) and TaCl$_2$(phenoxide)$_3$ fragments which form a binuclear structure using lone pairs from the oxo and chloro ligands. As such, the Ta(1) fragment is formally a 14-electron species and the Ta(2) fragment is a 12-electron species, but the ligands about each metal centre contribute additional electron density through π-bonds. The Ta(1)–Cl(2) bond length of 2.310(7) Å is significantly shorter than the two Ta(2)–Cl bonds in which the chloro ligands can only act as one-electron donors to Ta(2). Thus Ta(1) uses π-electron density from Cl(2) (as well as that from the two phenoxide ligands) to increase its electron count. It is interesting to note that the terminal chlorine can π-bond to the metal when lying *trans* to the 2-electron donor bridging oxo group. In high-valent monomeric complexes containing the terminal oxo ligand or the isoelectronic organoimido ligand, both of which act as 4-electron donors to the central atom, only lone pair donation from a ligand in the *trans* position has been observed.[20–23] However, in lower-valent complexes, chlorides are found *trans* to such ligands but in these cases the M–Cl bonds are considerably lengthened.[24,25]

A formal electron count for Ta(2) gives 12 electrons but this also is increased by π-electron density from the phenoxide ligands. The Ta(2)–O(6) bond distance (2.19(2) Å) is however significantly longer than the Ta(2)–O(4) and Ta(2)–O(5) distances (1.83(1) and 1.77(2) Å) so that the π-electron contribution comes mainly from O(4) and O(5).

The effect of phenoxide π-bonding on the *trans* ligand is also apparent in the molecule. About each tantalum centre the phenoxides are placed *trans* to ligands co-ordinating by σ-electron density only. The phenoxides orientate *cis* to one another which allows the metal atoms maximum use of oxygen π-electron density. *trans*-Orientated phenoxides would result in a competitive π-bonding situation leading to less effective use of the electron density available. This feature is similarly found in dialkylamido complex of tantalum(V). Crystal structure determinations of [Ta(NMe$_2$)$_3$Cl$_3$(NHMe$_2$)], [{Ta(NMe$_2$)Cl$_2$(NHMe$_2$)}O] and [Ta(NMe$_2$)$_3$Cl$_2$]$_2$ show the dimethylamido ligands are orientated *cis*.[26]

CONCLUSION

The studies show that when three of the chloro ligands in TaCl$_5$ are replaced by 2,6-di-alkylphenoxide ligands, octahedral geometry is possible when the alkyl substituents are isopropyl groups. However, when three or even two of the chloro ligands are replaced by 2,6-di-t-butylphenoxide ligands the steric size of the t-butyl substituents is sufficient to force a square-pyramidal geometry on the molecule. The results thus suggest that electronic effects are less important, the change in geometry apparently arising from steric factors alone.

EXPERIMENTAL

Lithium phenoxides were prepared by adding one equivalent of *n*-butyllithium to the phenol in petroleum ether and stirring for 2 h. Tantalum pentachloride was sublimed prior to use. Acetonitrile was dried over and distilled from calcium hydride. Petroleum ether (bpt range 40–60°), benzene and diethyl ether were distilled over sodium. All distillations were carried out under N$_2$ treated to remove oxygen and water, as were manipulations, using bench-top air sensitive techniques.[27] Infrared spectra were recorded on a Perkin–Elmer 597 spectrometer, ^{1}H NMR on a Varian T60 Model spectrometer and ^{13}C NMR spectra on a Jeol FX60 spectrometer. Analytical data were obtained by Prof. A. D. Campbell and Associates, University of Otago, New Zealand. Melting points were determined in sealed tubes under N$_2$ on an Electrothermal melting point apparatus and are uncorrected.

*Trichlorobis(*2,6 - *di* - *t* - *butylphenoxo)tantalum(V)* (1)

Lithium 2,6-di-t-butylphenoxide (3.2 g, 15.1 mmol) in benzene (50 cm^3) was added to a suspension of tantalum pentachloride (2.6 g, 7.3 mmol) in benzene (80 cm^3) and the mixture was stirred for 20 h. The orange solution was separated from the precipitate by centrifuging and the solvent removed to give an orange-red gum which was washed several times with petroleum ether. On drying *in vacuo* the complex was obtained as an orange powder. Yield: 3.6 g (71%). (Found: C, 48.6; H, 5.7%. C$_{28}$H$_{42}$Cl$_3$O$_2$Ta requires C, 48.2; H, 6.1%.)

IR(Nujol) bands at 1570w, 1370s, 1358s, 1252s, 1192s, 1175s, 1150s, 1104s, 1080s, 1020w, 915s, 895s, 864m, 819m, 790s, 780m, 732s, 688m, 670w, 630w, 568w, 538w, 519w, 460w, 440w, 354s, 345s and 300m cm^{-1}.

*Dichlorotris(*2,6 - *di* - *t* - *butylphenoxo)tantalum(V)* (2)

(a) A suspension of lithium 2,6-di-t-butylphenoxide (4.2 g, 19.8 mmol) in diethyl ether (100 cm^3) was added slowly to a suspension of tantalum pentachloride (2 g, 5.6 mmol) in diethyl ether (200 cm^3) and the reaction mixture was stirred for 3 days. The yellow solution was filtered and the solvent removed giving a yellow crystalline solid which was contaminated with an orange gummy substance. The product was extracted several times with petroleum ether (200 cm^3 in all) until the residue was no longer coloured yellow, the extracts were combined and the solvent removed. The resulting yellow orange gum was washed with acetonitrile (3 cm^3) leaving the complex as a yellow solid which was dissolved in petroleum ether (150 cm^3). The complex was obtained as yellow micro-crystals on reducing the solution volume and standing at -20°C. Yield: 2.3 g (48%). [M.p. 120–122°C] (Found: C, 57.8; H, 7.3; Cl, 7.8%. $C_{42}H_{63}Cl_2O_3Ta$ requires C, 58.1; H, 7.3; Cl, 8.2%.)

IR(Nujol) bands at 1570w, 1465m, 1420m, 1380s, 1358s, 1310w, 1258m, 1225m, 1194m, 1160s, 1088s, 1020w, 880s, 875s, 820m, 804w, 785m, 740s, 720w, 690m, 635w, 565w, 522w, 464w, 442w, 418w, 378w, and 320m cm^{-1}.

(b) A suspension of lithium 2,6-di-t-butylphenoxide (1 g, 1.43 mmol) in diethyl ether (50 cm^3) was added to trichloro*bis*(2,6-di-t-butylphenoxy) tantalum(V) (0.35 g, 1.64 mmol) in diethyl ether (100 cm^3) and the mixture was stirred for 2 days. The yellow solution was filtered, the solvent removed, and the residue extracted with petroleum ether (120 cm^3). The solution was filtered, the solvent removed, and the residue washed with acetonitrile (5 cm^3) leaving the complex as a yellow solid. Yield: 0.54 g (43%). The complex had identical m.p., IR, ^{13}C NMR spectra to the sample prepared under (a). Recrystallisation from benzene gave the complex as large yellow crystals.

Dichlorodiethylethertris(2,6-di-isopropylphenoxo) tantalum(V) (**4**)

Lithium 2,6-di-isopropylphenoxide (4.0 g, 21.6 mmol) in diethyl ether (100 cm^3) was added to tantalum pentachloride (2.5 g, 7.0 mmol) suspended in diethyl ether (150 cm^3) and the mixture was stirred for 36 h. The solution was filtered and the solvent removed to give a gum which failed to solidify. The product was dissolved in petroleum ether, the solution filtered, and the solvent removed to give the complex as a gummy material which failed to completely solidify even when held under vacuum for extended periods. Yield: 5.2 g (87%). (Found: Cl, 8.0%. $C_{40}H_{61}Cl_2O_4Ta$ requires: Cl, 8.3%.) The complex was further characterised by spectral properties.

IR (Nujol) bands at 1600w, 1490s, 1335s, 1262s, 1200s, 1152m, 1110m, 1065w, 1050m, 1020w, 930s, 902m, 985w, 830m, 800s, 755s, 720s, 660w, 610w, 550w, 510w, 440w, 320m and 295m cm^{-1}.

Chloro(μ-dichloro)penta(2,6-di-isopropylphenoxo) (μ-oxo)ditantalum(V) (**6**)

Air was admitted to a solution of dichlorodiethylethertris(2,6-di-isopropylphenoxy)tantalum(V) in petroleum ether. The flask was stoppered and allowed to stand at -20°C whereupon a small quantity of yellow crystals was formed. The complex was filtered, washed with petroleum ether, chilled to ice temperature and dried *in vacuo*. Characterisation was made by X-ray crystallography.

Crystallographic studies

Single crystals of [$TaCl_2$(2,6-di-t-butylphenoxide)$_3$] (**2**) and [$Ta_2Cl(\mu\text{-}Cl)_2$(2,6-di-isopropylphenoxide)$_5(\mu\text{-}O)$] (**5**) were grown from benzene and toluene solutions respectively and sealed under nitrogen in glass capillaries. They were mounted on an Enraf-Nonius CAD-4 diffractometer.

Crystal data: *Complex* (**2**). $C_{42}H_{63}Cl_2O_3Ta$, $M = 866.8$, monoclinic, $a = 18.902(6)$ Å, $b = 10.815(8)$ Å, $c = 20.259(4)$ Å, $\beta = 92.62(2)°$, $U = 4137.1$; space group $P2_1/c$, $Z = 4$, $D_c = 1.392$ g cm^{-1}, $F(000) = 1784$, $\mu(\text{Mo-}K_\alpha) = 29.6$ cm^{-1}.

Crystal data: *Complex* (**5**). $C_{60}H_{85}Cl_5O_6Ta_2$, $M = 1440.2$, monoclinic, $a = 11.174(1)$ Å, $b = 20.402(3)$ Å, $c = 27.143(3)$ Å, $\beta = 94.57(1)°$, $U = 6168.2$; space group $P2_1/c$, $Z = 4$, $D_c = 1.551$ g cm^{-1}, $F(000) = 2896$, $\mu(\text{Mo-}K_\alpha) = 40.0$ cm^{-1}.

Data collection. Accurate unit cell parameters were determined by least-squares fits to the setting angles of 25 reflections measured using Mo-K_α ($\lambda = 0.71069$ Å) radiation. Data collection was by $2\theta/\omega$ scans with a background/peak count-time ratio of 1/2. For complex (**2**) reflections were counted for 60 s or until $\sigma(I)/I$ was 0.02, a total of 6258 reflections being measured to $\theta_{\max}$ of 22°. The intensity of three reflections monitored throughout the collection showed an isotropic decline with time. For complex (**5**) decomposition in the X-ray beam was more severe and the maximum count time was reduced to 40 s. Even so, it was necessary to use four crystals to measure 2567 reflections to $\theta_{\max}$ of 19°.

The data were corrected for Lorentz, polarisation, crystal decay and absorption.[28] Each crystal for (**5**) was treated separately and the data placed on a common scale by comparison of common reflections. Subsequently separate scale factors were refined for each crystal.

Structural solutions and refinements. Both structures were solved by Patterson and Fourier methods and refined by the full-matrix least-squares technique. Computing was carried out using the SDP suite of programs on a PDP-11 computer and SHELX-76 in an IBM 4341 computer. The function minimised was $\Sigma w(|F_o|-|F_c|)^2$. Atomic scattering factors and dispersion corrections were for neutral atoms. After initial isotropic refinement, anisotropic thermal parameters were refined for the heavier atoms. Final residuals R and R_w were 0.063 and 0.061 for the 1690 observed data of complex (**2**) and 0.062 and 0.068 for the 3693 observed data of complex (**5**).

Final atomic coordinates for both complexes, tables of thermal parameters, and listings of observed and calculated structure factors have been deposited with the Editor as supplementary material.*

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* Atom coordinates for these structures have also been deposited with the Cambridge Crystallographic Data Centre for inclusion in their Data Base. Copies are available on request from the Editor at Queen Mary College.