

## The molecular structure of the mixed chloro-iodo-titanium(II) complex, $(\eta^6\text{-durene})\text{Ti}[(\mu\text{-X})_2(\text{AlX}_2)]_2$ ( $\text{X} = \text{Cl}, \text{I}$ ); the distribution of the halogen atoms in the bridge and the outer positions

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### Abstract

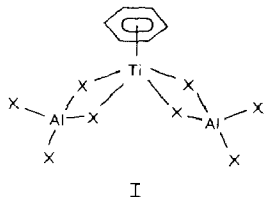
The titanium(II) complex  $(\eta^6\text{-durene})\text{TiAl}_2\text{Cl}_{8-y}\text{I}_y$  (II) crystallizes in the rhombic space group  $Pna2_1$  with  $Z = 4$  and lattice parameters  $a$  19.949(6),  $b$  9.146(4),  $c$  13.883(7) Å. The titanium atom in II possesses square pyramidal coordination similar to all of the known structures of arenetitanium(II) complexes; four halogen atoms form the corners of a square and the  $\pi$ -bonded durene takes the axial position. An X-ray diffraction study gave a value of  $y = 3.25$  for II. The halogen ligands were not randomly distributed: about 85% of the iodine ligands were found to be in the outer positions. The aromatic plane of apical 1,2,4,5-tetramethylbenzene (durene) is nearly parallel to the plane of the bridging halogen (largely chlorine) atoms; the durene molecule is oriented so that the pseudosymmetrical plane of the complex through the Al(1), Ti and Al(2) atoms bisects the C(1)–C(2) and C(4)–C(5) bonds. The methyl groups are bent by an average of 0.18 Å above the aromatic ring plane.

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### Introduction

The arenetitanium(II) complexes (I) are well-defined, thermally stable complexes which are excellent catalysts for the specific cyclotrimerization of butadiene [1,2] and the dimerization of cycloheptatriene [3]. The crystal and molecular structures of  $(\eta\text{-C}_6\text{H}_6)\text{Ti}(\text{AlCl}_4)_2$  (Ia) and  $(\eta\text{-C}_6\text{Me}_6)\text{Ti}(\text{AlCl}_4)_2 \cdot \text{C}_6\text{H}_6$  (Ib) were first determined by Thewalt et al. [4,5]. Recently, the structures of the  $(\eta\text{-C}_6\text{H}_6)\text{Ti}(\text{AlCl}_4)_2$

$\cdot C_6H_6$  (Ic) [6],  $(\eta-C_6H_6)Ti(AlBr_4)_2 \cdot C_6H_6$  (Id) and  $(\eta-C_6H_6)Ti(AlI_4)_2$  (Ie) complexes were determined by Troyanov et al. [7]. All these arenitetanium(II) complexes possess square-pyramidal coordination around the central titanium atom: the four halogen atoms form the pyramid base and an  $\eta$ -arene ligand occupies the apex. Differing geometries of the  $Ti(\mu-X)_2Al$  bridging bonds have been observed, depending on the nature of the halogen ligands [4–7].



The catalytic properties of the benzenetitanium(II) complexes in the cyclotrimerization of butadiene were found to be strongly dependent on the type of halogen atom. The chloro complex Ia typically shows a rate constant of butadiene consumption,  $k_{app}$ , of  $75 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$  and negligible deactivation; the bromo complex Id shows an much higher initial rate,  $k_{app} = 210 \text{ l}^2 \text{ mol}^{-2} \text{ s}^{-1}$ , but rapidly becomes deactivated. The mixed, iodine-containing complexes were practically inert. However, the mixed chloro-bromo complexes  $(\eta-C_6H_6)TiAl_2Cl_{8-x}Br_x$  ( $x \leq 4$ ) exhibited a higher initial reaction rate than that shown by the chloro complex, while its deactivation remained low [1]. The high stability of the complexes is tentatively ascribed to the presence of chlorine atoms in the bridge positions. To determine the distribution of the halogen atoms in these complexes, the complexes were studied by electronic absorption spectroscopy and, indirectly by ESR [8] after the benzenetitanium(II) complexes had been converted into the  $CpTi^{III}$  complexes by reaction with monomeric cyclopentadiene. The deviation from linearity of the dependence of the position of a  $d-d$  absorption band of the  $(C_6H_6)Ti^{II}$  complexes and of the  $g$ -value of the  $CpTi^{II}$  complexes on the Cl-to-Br ratio in the complexes suggests that the chlorine ligands favoured the bridge positions compared with the random distribution. Since the same effect should be more pronounced in the mixed chloro-iodo complexes, we attempted to determine the distribution of the halogen ligands in the  $(\eta^6\text{-durene})TiAl_2Cl_{8-y}I_y$  (II) complex containing approximately equal amounts of the two halogens. The structure of the durene ligand and its orientation with respect to the inorganic skeleton was also examined.

## Experimental

### *Synthesis of $(\eta^6\text{-durene})TiAl_2Cl_{8-y}I_y$ (II)*

Complex II was prepared by the general Fischer–Hafner method [9]; the procedure, starting materials, and solvents used in the synthesis have been described elsewhere [10]. A mixture of  $AlI_3$  (15.4 g, 38 mmol), Al powder (2 g, 70 mmol),  $TiCl_4$  (3.3 ml, 30 mmol) and durene (4 g, 30 mmol) in benzene (100 ml) was refluxed under argon for 25 h. The red-violet solution was separated from the residue of metallic aluminium. The violet crystalline material was precipitated out by addition of hexane and separated from the mother liquor. The Cl/I molar ratio in the crystalline complex was found to be  $1.38 \pm 0.05$  by chemical analysis. The electronic absorption spectrum of II in benzene solution consisted of a charge

transfer band with high intensity at 393 nm and low intensity bands at 564 and 830 nm (for the spectra see refs 10,11). The crystalline complex, II, was dissolved in benzene and small crystals suitable for crystallography were isolated from a saturated benzene–hexane solution.

### Crystal structure determination of II

A dark violet crystal of II (0.2 × 0.4 × 0.4 mm), highly sensitive to oxygen and moisture, was placed in a glass capillary tube in a glove box under argon and the tube was sealed. The complex crystallizes in the rhombic space group  $Pna2_1$  with cell constants  $a$  19.949(6),  $b$  9.146(4),  $c$  13.883(7) Å,  $V$  2533 Å<sup>3</sup>, and  $Z = 4$ . Diffraction data were collected on a CAD-4 four-circle automatic diffractometer with monochromatized Mo- $K_\alpha$  radiation. A total of 2316 independent reflections were measured; 1050 reflections with  $I > 3\sigma(I)$  were used for solution of the structure by use of SDP programs. The intensities of the reflections were corrected for absorption from the PSI-scans of 8 reflections. The structure was solved by direct methods with the MULTAN-82 program; the coordinates of several Cl atoms and all the C atoms were determined by subsequent Fourier syntheses. During the refinement of the positional and thermal parameters of the halogen atoms initially assigned as chlorine or iodine atoms, it was found that only chlorine atoms were present in some of the positions, while randomly distributed Cl and I atoms were present in other positions. It followed from the several attempted combinations for

Table 1

Atom coordinates ( $\times 10^4$  for Cl, X1, X2, Ti, Al and  $\times 10^3$  for C) and equivalent isotropic temperature factors for II<sup>a</sup>

Atom	$x$	$y$	$z$	$B$ (Å <sup>2</sup> )
Ti	6025(3)	209(6)	2900(4)	4.1(1)
Al(1)	5468(5)	3200(10)	1491(8)	5.6(3)
Al(2)	7293(5)	-1710(10)	1557(8)	6.0(3)
X1(1)	7462(2)	498(5)	2627(3)	8.0(1)
X1(2)	7896(2)	-3797(4)	2233(3)	8.10(9)
X2(1)	6052(1)	3962(4)	0	6.87(7)
X2(2)	4485(2)	4667(4)	1942(3)	7.75(8)
X2(3)	7544(2)	-1142(4)	-116(3)	7.48(7)
Cl(1)	5149(4)	821(9)	1463(5)	5.1(2)
Cl(2)	6203(5)	3061(8)	2695(6)	5.7(2)
Cl(3)	6207(4)	-2040(9)	1722(6)	5.6(2)
C(1)	547(2)	106(4)	444(2)	5.4(7)
C(2)	500(2)	18(4)	394(2)	5.3(7)
C(3)	517(2)	-126(4)	377(2)	5.4(8)
C(4)	581(2)	-184(4)	401(2)	5.6(8)
C(5)	629(2)	-93(4)	451(2)	6.1(8)
C(6)	612(2)	58(4)	466(2)	5.6(8)
C(11)	530(2)	259(5)	480(3)	10(1)
C(21)	429(2)	72(5)	370(3)	9(1)
C(41)	595(2)	-357(4)	389(3)	7(1)
C(51)	693(2)	-163(4)	492(3)	8(1)

<sup>a</sup> Equivalent isotropic temperature factors  $B_{\text{iso}}^{\text{equiv}} = \left(\frac{4}{3}\right)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3)]$ ; X1 = 0.5 Cl + 0.5 I, X2 = 0.25 Cl + 0.75 I.

Table 2

Bond distances in II (Å)

Ti–Cl(1)	2.710(10)	Ti–C(3)	2.48(3)
Ti–Cl(2)	2.649(9)	Ti–C(4)	2.47(3)
Ti–Cl(3)	2.653(10)	Ti–C(5)	2.52(3)
Ti–X1(1)	2.904(6)	Ti–C(6)	2.47(3)
Al(1)–Cl(1)	2.270(14)	C(1)–C(2)	1.41(5)
Al(1)–Cl(2)	2.228(14)	C(2)–C(3)	1.38(5)
Al(1)–X2(1)	2.469(11)	C(3)–C(4)	1.42(5)
Al(1)–X2(2)	2.455(11)	C(4)–C(5)	1.45(5)
Al(2)–Cl(3)	2.200(13)	C(5)–C(6)	1.43(5)
Al(2)–X1(1)	2.528(12)	C(1)–C(6)	1.41(5)
Al(2)–X1(2)	2.444(12)	C(1)–C(11)	1.53(6)
Al(2)–X2(3)	2.432(12)	C(2)–C(21)	1.53(6)
Ti–C(1)	2.53(3)	C(4)–C(41)	1.61(5)
Ti–C(2)	2.50(4)	C(5)–C(51)	1.54(5)

Table 3

Main bond angles (°) in II

Cl(1)TiCl(2)	78.7(3)	X1(2)Al(2)X2(3)	115.6(5)
Cl(1)TiX1(1)	121.4(3)	TiCl(1)Al(1)	90.3(4)
Cl(3)TiX1(1)	81.6(2)	TiCl(2)Al(1)	92.9(4)
Cl(2)TiCl(3)	132.8(3)	TiCl(3)Al(2)	95.3(4)
Cl(1)Al(1)Cl(2)	98.1(5)	TiX1(1)Al(2)	82.7(3)
X2(1)Al(1)X2(2)	115.9(5)	C–C–C	120±3
Cl(3)Al(2)X1(1)	100.4(5)		

different statistical weights of the halogen atoms in various positions, that the structure can be solved by the use of two types of “mixed halogen atoms” whose atomic scattering factors were defined as follows: X1 = 0.5 Cl + 0.5 I and X2 = 0.25 Cl + 0.75 I. The least-squares structural refinement was isotropic for all the carbon atoms and anisotropic for all the halogen (Cl, X1, X2), titanium and aluminium atoms. The final agreement factor (*R*) was 0.053. The positions of the hydrogen atoms were not determined. The atom coordinates are listed in Table 1; bond lengths and valence angles are given in Tables 2 and 3, respectively.

## Results and discussion

The structure of II is similar to that of the known structures for the complexes Ia–Ie formulated as  $(\eta^6\text{-arene})\text{TiAl}_2\text{X}_8$  (X = Cl, Br, I; arene = C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>Me<sub>6</sub>) [4–7]. The composition of II, (C<sub>6</sub>H<sub>2</sub>Me<sub>4</sub>)TiAl<sub>2</sub>Cl<sub>4.75</sub>I<sub>3.25</sub> was determined from an X-ray diffraction study in which different atomic scattering factors were used for “mixed halogen atoms” X1 and X2 in positions containing both types of halogen atoms in the appropriate proportions. The structure of II showing positions of the “mixed halogen atoms” X1 and X2 and orientation of the durene ligand with respect to the

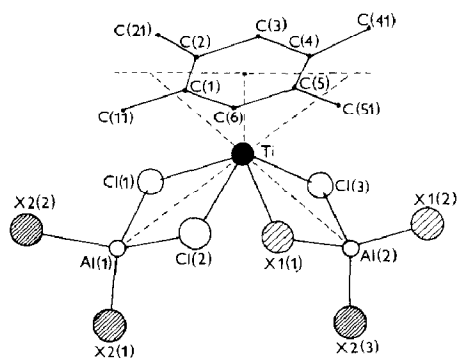


Fig. 1. Crystal structure of  $(\eta^6\text{-durene})\text{-TiAl}_2\text{Cl}_{8-\gamma}\text{I}_\gamma$  ( $\gamma = 3.25$ ) (II) showing the molecular geometry and atom numbering scheme.

inorganic skeleton of the complex is depicted in Fig. 1. Three chlorine atoms and one “mixed” X1 atom occupy the bridge positions while three “mixed” X2 atoms and one X1 are situated in the outer positions. Thus most of the iodine atoms (85%) occupy the outer positions while the chlorine atoms strongly prefer the bridge positions.

The average length of the Ti–Cl bond, 2.66 Å, is close to the length of that in the chloro-only complexes [4–6]. The lengths of the bridging Ti–X1 and Al–X1 bonds are 2.90 Å and 2.53 Å, respectively, slightly shorter than those in  $(\text{C}_6\text{H}_6)\text{TiAl}_2\text{I}_8$  (Ie) which are 2.95–3.00 and 2.57–2.58 Å, respectively [7]. The outer bonds, Al–X1 and Al–X2, with an average length of 2.45 Å are also slightly shorter than the outer bonds in Ie (2.49 Å). The bridging cycles  $\text{TiClAlX1}$  and  $\text{TiClAlCl}$  are planar, which is consistent with the structure of the bromo complex Id, but at variance with the structures of the chloro (Ia, Ib and Ic) and iodo (Ie) complexes in which the cycles are bent around the halogen–halogen connecting line [6,7]. The approximately rectangular pyramid base formed by Cl(1), Cl(2), Cl(3) and X1(1) is parallel to the aromatic ring plane (within 2°): the Cl(2) and Cl(3) atoms are  $\sim 0.15$  Å closer to, and the Cl(1) and X1(1) atoms are  $\sim 0.15$  Å further away from, the aromatic ring plane. Similar deviations of the base and aromatic ring planes from parallelism have been observed for other arenetitanium(II) complexes [6,7]. The average titanium–base distance is 1.22 Å.

The average Ti–C bond distance 2.50 Å is similar to those in other arenetitanium(II) complexes, and is independent of the nature of the halogen atom. The aromatic ring plane C(1)–C(6) is orientated so that the pseudosymmetry plane of the complex through the Ti, Al(1) and Al(2) atoms bisects the C(1)–C(2) and C(4)–C(5) bonds. The methyl groups of durene are bent away from the aromatic ring plane so that their carbon atoms lie an average of 0.18 Å above the aromatic plane (they are farther from titanium). This observation is consistent with the results reported by Thewalt for the  $\text{C}_6\text{Me}_6$  complex Ib [5]. The orientation of the  $\text{C}_6\text{Me}_6$  molecule with respect to the plane of the complex is similar to that for our complex and both methyl groups on C(3) and C(6) (by our notation) of the durene are bent slightly towards the titanium atom, whereas those on C(1), C(2), C(4) and C(5) are bent out of the ring plane in the opposite direction (by 0.09–0.22 Å). Since there is little steric interaction between the durene or hexamethylbenzene ligands and the inorganic skeleton of complexes II and Ib, the reason for the identical orientations

and deformed geometries of the two ligands lies in the directional electronic interaction between the titanium and arene orbitals.

The X-ray diffraction study of II confirms that chlorine atoms favour coordination to titanium in the bridge positions, which is consistent with similar conclusions down from spectroscopic studies performed previously on a series of mixed chlorobromo benzenetitanium(II) complexes [8]. This is in contrast to systems where separate Ti and Al halides are formed; e.g.,  $TiI_3$  of 99% purity was obtained from the reduction of  $TiCl_2I_2$  with  $Et_2AlI$  [12]. In the arene complexes, however, the presence of chlorine atoms in the bridge bonds enhances the stability of the Al-Ti-Al complexes.

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