The Crystal Structure of Chloro-π-cyclopentadienylbis-8-quinolinolatotitanium(IV)

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Summary The structure of chloro-π-cyclopentadienylbis-8-quinolinolatotitanium(IV) can be described either as a distorted octahedral species with a unidentate π-cyclopentadienyl group or as an eight-co-ordinate species with a tridentate π-cyclopentadienyl group.

CHLORO-π-CYCLOPENTADIENYLBIS-8-QUINOLINOLATOTITANIUM(IV), $TiCl(C_5H_5)ox_2$, can be prepared by the direct action of 8-quinolinol (oxH) on dichlorodi-π-cyclopentadienyltitanium(IV), $TiCl_2(C_5H_5)_2$, in acetonitrile at room temperature.[1] This compound is a member of the series of compounds of general formula $MX(C_5H_5)(chelate)_2$, where M = Ti, Zr or Hf; X = Cl, Br, or I and chelate = 8-quinolinol, acetylacetone, benzoylacetone, or dibenzoylmethane. Many of these compounds have now been prepared by the same direct method mentioned above for $TiCl(C_5H_5)ox_2$, and although some have been reported elsewhere,[2] the amount of structural information available is very limited. $TiCl(C_5H_5)ox_2$ is closely related to $TiCl_2ox_2$ whose structure has been determined[3] and it was considered of interest to study the effect of replacing a chlorine atom by a cyclopentadienyl group.

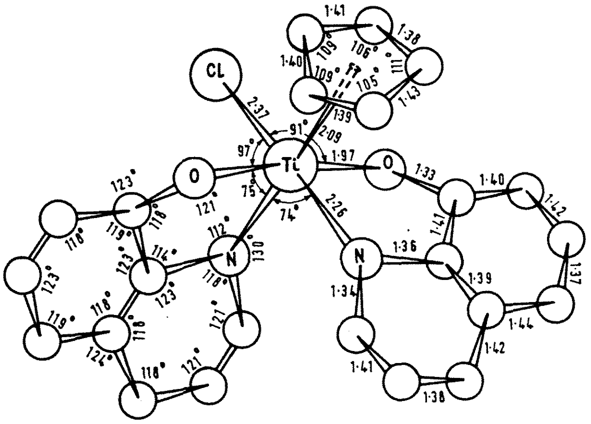
It has been shown from *X*-ray powder photographs that the compounds $MX(C_5H_5)ox_2$ (M = Ti,Zr; X = Cl,Br) are isomorphous, while cryoscopic molecular weight and electrolytic conductance measurements indicate that they are monomeric non-electrolytes.[1] Crystal data for $TiCl(C_5H_5)ox_2$: bright red crystals from dichloromethane, monoclinic,

$a = 8{\cdot}82$, $b = 13{\cdot}85$, $c = 16{\cdot}80$ Å, $\beta = 111{\cdot}7°$; $U = 1906{\cdot}8$ Å^3, $D_m = 1{\cdot}50$ g.cm.$^{-3}$ (by flotation), for $Z = 4$, $D_c = 1{\cdot}52$ g.cm.$^{-3}$, Cu-K_α radiation, $\mu = 54{\cdot}3$ cm.$^{-1}$, space group $P2_1/c$ (No. 14, C^5_{2h}). 2402 independent observable reflections were estimated visually from equi-inclination Weissenberg photographs taken about all three crystallographic axes.

The titanium atom and its co-ordination sphere were located in a three-dimensional Patterson synthesis and the other atoms, excluding hydrogens, were found from a three-dimensional electron density map. Refinement by block-diagonal least-squares with anisotropic temperature factors for all atoms has resulted in an agreement index R of 0·112.

The stereochemistry of the molecule, together with bond lengths and angles, is shown in the Figure. The chemically equivalent bond lengths and angles do not differ significantly and average values are quoted. The estimated standard deviations of the bond lengths vary from 0·005 Å, for bonds involving titanium, to 0·020 Å for C–C bonds and those of the angles from 0·25° to 1·40°. The 8-quinolinol groups and the cyclopentadienyl group are planar within the limit of the experiment.

The Ti–Cl bond length of 2·37 Å suggests[3,4] a co-ordination number for the titanium greater than six, possibly eight, This would support the hypothesis that the π-cyclopentadienyl group is behaving as a tridentate ligand. The Ti–O bond, 1·97 Å, and the Ti–N bond, 2·26 Å, as found previously,[3] differ in length by more than 0·25 Å. There is as yet no satisfactory explanation for this large difference.



(*Received, May 20th,* 1969; *Com.* 719.)

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