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The Structure of Dichlorodi-8-quinolinolatotitanium(IV)

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Titanium tetrachloride reacts with 8-quinolinol in 1 : 2 mole ratio to form the adduct $TiCl_4$, 2OxH (OxH = 8-quinolinol, Ox = 8-quinolinolato), from which two moles of HCl can be eliminated to produce $TiCl_2Ox_2$. This compound is a member of a large group of compounds of general formula $MX_2(chelate)_2$ where M can be Ti, Ge, or Sn; X = F, Cl, Br or I, and 'chelate' can be 8-quinolinolato, acetylacetonato, or salicylaldehydato. I.r.[1] and n.m.r.[2] examinations have been made in an attempt to determine the configuration of these molecules but no crystallographic information is available.

The $TiCl_4$–8-quinolinol system is capable of yielding several products in addition to $TiCl_2Ox_2$, *e.g.*, $TiCl_4OxH$, $TiCl_4$,2OxH, $TiClOx_3$, and $TiCl_3Ox$ have all been isolated.[3] It would be of interest to study the mechanism of the reactions leading to such varied products and to the interchange of these products but such a study is seriously hindered by the paucity of structural information. We are therefore examining some of these compounds by *X*-ray crystallographic methods and report here a preliminary description of the complex $TiCl_2Ox_2$.

It has previously been shown[3] by *X*-ray powder patterns that MCl_2Ox_2 complexes of Ti, Ge, and Sn are isomorphous and that the compounds TiX_2Ox_2 are isomorphous for X = Cl and Br. It has been suggested from i.r. studies[1] that $TiBr_2Ox_2$ is *trans* with respect to the bromine. We show, however, that $TiCl_2Ox_2$ is undoubtedly *cis* with respect to chlorine.

Crystals of $TiCl_2Ox_2$, recrystallised by sublimation, are monoclinic with cell dimensions a = 14·06 Å, b = 8·54 Å, c = 14·97 Å, and β = 111°. D_m = 1·64 g.cm.$^{-3}$ (by flotation), for Z = 4, D_c = 1·61 g.cm.$^{-3}$. Systematic absences indicate space group $C2/c$ or Cc but after working in both space groups we conclude that $C2/c$(No. 15, C_{2h}^6) is probably correct.

The titanium and its immediate co-ordination sphere were located from a three-dimensional Patterson and the rest of the molecule, except hydrogen atoms, was then found in a difference

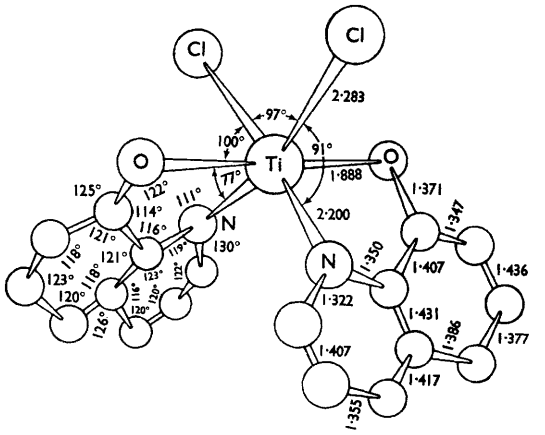

Figure. *Molecular structure of* $TiCl_2Ox_2$ *showing bond lengths and angles.*

electron-density map. The structure was refined by block diagonal and full matrix least-squares methods with anisotropic temperature factors.[4] The R factor is now 0·116 for 1394 independent non-zero reflections estimated visually from Weissenberg films taken about all three crystallographic axes. The Figure shows the stereochemistry of the molecule which has a crystallographic two-fold axis through the titanium atom, bisecting the Cl–Ti–Cl angle and the N–Ti–N angle. The figure also gives the bond lengths and angles, the estimated standard deviations of the bond lengths are between 0·01 and 0·025 Å while those of the angles are about 1°. The quinolinolate groups are planar within the limits of the experiment and the bond lengths do not differ significantly from those calculated for the 8-quinolinol molecule.[5]

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