# On Supposedly Five-co-ordinate Titanium(IV) Complexes. The Crystal and Molecular Structure of $Cl_3Ti(C_5H_7O_2)$

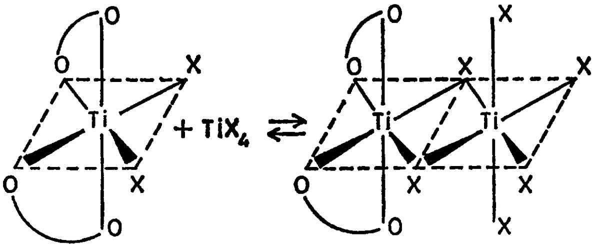
By N. Serpone,* P. H. Bird, and D. G. Bickley
(*Department of Chemistry, Sir George Williams University, Montreal* 107, *Canada*)
and D. W. Thompson
(*Department of Chemistry, College of William and Mary, Williamsburg, Virginia* 23185)

*Summary* An *X*-ray diffraction study shows that the titanium(IV) complex, $Cl_3Ti(C_5H_7O_2)$, of apparent five-co-ordinate stoicheiometry is, in the solid state, a centrosymmetric chlorine-bridged dimer in which each titanium atom is six-co-ordinate and carries a bidentate acetylacetonate ($C_5H_7O_2^-$) ligand.

Titanium(IV) complexes of the type $X_3Ti(dik)$ (where dik is a $\beta$-diketonate ligand, *e.g.*, $C_5H_7O_2^-$ = acetylacetonate, and X is a halogen or an alkoxy-group), have an apparent five-co-ordinate stoicheiometry which has recently been the subject of some interest. Mehrotra *et al.*[1] pointed out both the apparent five-co-ordinate nature of trialkoxy-($\beta$-diketonato)titanium(IV) complexes and their disproportionation according to reaction (1). Thompson, Somers, and

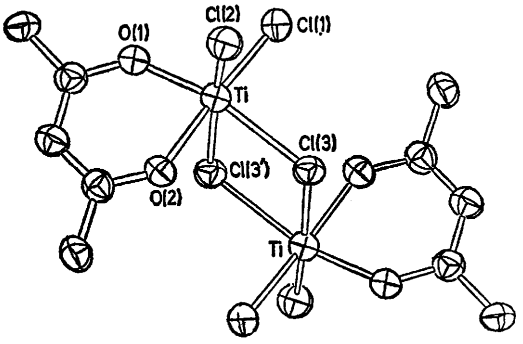
$$2(RO)_3Ti(dik) \rightleftharpoons (RO)_2Ti(dik)_2 + Ti(OR)_4 \qquad (1)$$

Workman[2] reported that the complexes $X_3Ti(C_6H_9O_2)$ (where X = Cl, Br; and $C_6H_9O_2$ is the anion of 3-methylpentane-2,4-dione) are non-electrolytes and monomeric in nitrobenzene, but they were unable from n.m.r. studies to deduce the stereochemistry of these species in solution. More recently, on the basis of n.m.r. evidence, Holloway and Sentek[3] suggested that the apparently five-co-ordinate trialkoxy(acetylacetonato)titanium(IV) compounds are actually 1:1 mixtures of the more familiar six-co-ordinate $(RO)_2Ti(C_5H_7O_2)_2$ and four-co-ordinate $Ti(OR)_4$ derivatives



(2)

which are weakly associated in solution according to a reaction which they depicted as (2). Support for such a dimeric structure was adduced from the behaviour of trichloro(acetylacetonato)titanium(IV).[3] Thompson *et al.*[4] have synthesized several of these $X_3Ti(dik)$ complexes (where X = Cl, Br; and dik are various $\beta$-diketonate ligands) which are non-electrolytes and monomeric in nitrobenzene and benzene; in particular, $Cl_3Ti(C_{10}H_9O_2)$ (where $C_{10}H_9O_2^-$ is the anion of 1-phenylbutane-1,3-dione) was characterized and evidence was presented[4] which was claimed to be consistent with this complex having a five-co-ordinate structure (in solution) and participating in an equilibrium of the type shown in reaction (1). We have undertaken an *X*-ray structural study on trichloro(acetylacetonato)titanium(IV) to clarify the situation.



FIGURE

The compound was prepared by direct reaction of $TiCl_4$ and acetylacetone (1:1 molar ratio) in dry benzene under a nitrogen atmosphere. Recrystallization from dry dichloromethane yielded elongated dark red crystals; space group $P2_1/n$ (No. 14); $a = 8{\cdot}381(5)$, $b = 10{\cdot}734(5)$, $c = 10{\cdot}517(6)$ Å, $\beta = 93{\cdot}92(3)°$, $Z$ for $Cl_3Ti(C_5H_7O_2) = 4$. Diffraction data were collected on a Picker automatic *X*-ray diffractometer. Subsequently, 1092 reflections with intensities greater than $3\sigma(I)$ were used in the solution of the structure by conventional Patterson and Fourier techniques. Full-matrix least-squares refinement of all non-hydrogen atoms with anisotropic thermal parameters reduced the final discrepancy index to 4·2%.

The molecular geometry is depicted in the Figure. The complex is the dimer $[Cl_3Ti(C_5H_7O_2)]_2$ with two chlorine atoms bridging the titaniums, but the space group requires it to be centrosymmetric and not as depicted in reaction (2). Bond lengths to each titanium atom are: Ti–Cl(1), 2·248(2); Ti–Cl(2), 2·217(2); Ti–Cl(3), 2·419(2); Ti–Cl(3′), 2·569(2); Ti–O(1), 1·883(4); Ti–O(2), 1·964(4) Å. There are thus significant differences between all four Ti–Cl distances and between the two Ti–O distances, as might be expected from the low symmetry of co-ordination at titanium. The Ti–Ti distance is 3·774(3) Å and the Cl(3)–Cl(3′) distance is 3·264(4) Å.

I.r. spectra were recorded on both a Perkin-Elmer model 225 (KBr plates) and a Beckman IR-11 (polyethylene plates) spectrophotometer. The solid state far-i.r. spectra (500—150 cm$^{-1}$) of $[Cl_3Ti(C_5H_7O_2)]_2$ reveal bands at 486, 420, 399, 322, 276, 246, 199, and 165 cm$^{-1}$; the strong band at 399 cm$^{-1}$ is assigned to the terminal Ti–Cl stretching mode. In the far-i.r. spectrum of $Ti(C_5H_7O_2)_2Cl_2$, bands have been reported[5] at 474s,b, 413w, 389sh, 378s, 317m, 265w, and 222w cm$^{-1}$ with the Ti–Cl stretching vibrations being assigned to the bands at 378 and 389 cm$^{-1}$. Comparison between the two spectra suggests that the bands at 276 and 246 cm$^{-1}$ for $[Cl_3Ti(C_5H_7O_2)]_2$ are probably due to bridging Ti–Cl stretching modes, in keeping with earlier work[6] on the $[Et_4N][Ti_2Cl_9]$ complex for which bridging Ti–Cl stretching vibrations were observed at 268 and 230 cm$^{-1}$.

Support of this research by the National Research Council of Canada is acknowledged.

(*Received*, *6th December* 1971; *Com.* 2082.)

---

[1] D. M. Puri and R. C. Mehrotra, *J. Less-Common Metals*, 1961, **3**, 247; *ibid.*, 1963, **5**, 2; D. M. Puri, K. C. Pande, and R. C. Mehrotra, *ibid.*, 1962, **4**, 481.
[2] D. W. Thompson, W. A. Somers, and M. O. Workman, *Inorg. Chem.*, 1970, **9**, 1252.
[3] C. E. Holloway and A. E. Sentek, *Canad. J. Chem.*, 1971, **49**, 519.
[4] D. W. Thompson, R. W. Rosser, and P. B. Barrett, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 931.
[5] R. N. Lowry, Ph.D. Thesis, Cornell University, Ithaca, New York, 1969.
[6] J. A. Creighton and J. H. S. Green, *J. Chem. Soc.* (*A*), 1968 ,808.