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The Crystal Structure of $(TiCl_4 . POCl_3)_2$

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The crystal structure of $(TiCl_4 \cdot POCl_3)_2$ has been determined from three-dimensional X-ray data. The structure is built up of dimeric molecules $(TiCl_4 \cdot POCl_3)_2$ with double chlorine bridges between the two titanium atoms of the dimer. The coordination around the titanium atom is octahedral. The oxygen atom in $POCl_3$ functions as donor atom. The approximately tetrahedral structure of $POCl_3$ is preserved.

Titanium tetrachloride is a strong Lewis acid and forms a great number of addition compounds with different donor molecules (Lewis bases). The mole ratio acceptor molecule to donor molecule is 1:1 or 1:2. The phase diagram $TiCl_4$—$POCl_3$ shows the existence of both types of compounds between $TiCl_4$ and $POCl_3$.[1] Sheldon and Tyree [2] have concluded from the shifts in the phosphoryl bond stretching frequency (measured in infrared) that phosphoryl chloride functions as a donor molecule through the oxygen atom. The present study was undertaken as a part of our investigations of the coordination and of the chemical bonds in addition compounds of different oxychlorides.

PREPARATIONS

Single crystals of the very hygroscopic compound were prepared in sealed capillary tubes by a method of zone melting. In most preparations the compound studied in this paper was obtained. Two other compounds appeared, however, in some cases. The unit cell volumes of those two crystals show simple ratios to the unit cell volume of the crystals usually prepared *(vide infra)*. They therefore probably represent other modifications. Preparations from carbon tetrachloride solutions give only the most common modification. We have not further studied the conditions of preparation of the two less common modifications.

CRYSTAL DATA

The unit cell dimensions of the orthorhombic crystals were determined by an extrapolation method used earlier by Hermodsson and Strandberg [3]. The values are $a = 12.42 \pm 0.02$ Å, $b = 12.76 \pm 0.05$ Å and $c = 13.51 \pm 0.02$ Å. The extinctions $h0l$ for l odd, $0kl$ for k odd and $hk0$ for h odd lead to the spacegroup *Pbca*.

This is in agreement with the data published earlier [1,4] except for some small corrections and improvements in accuracy. They also showed that there are eight units of $TiCl_4 \cdot POCl_3$ in the unit cell.

The other two modifications are monoclinic with the following approximate unit cell dimensions:

$a = 9.9$ Å, $b = 8.7$ Å, $c = 12.3$ Å and $\beta = 98°$
$a = 13.9$ Å, $b = 12.1$ Å, $c = 19.1$ Å and $\beta = 105°$

The cell volumes are very nearly one and three halves respectively of the orthorhombic unit cell volume (0.48 and 1.43).

The single crystal was rotated around the *b*-axis and Weissenberg photographs were taken. Nine zones (0—8) were recorded with Ni-filtered Cu-*K* radiation using multiple-film technique. Connection between the zones was obtained using a method described by Magnéli [5].

The 785 independent intensities were estimated visually. The relative $|F|^2$ values were obtained after correction using the chart of Lu [6]. No correction was made for absorption errors. The capillary tube used had an inner diameter of 0.10 mm. The linear absorption coefficient is 236.0 cm^{-1} for Cu-$K\alpha$ radiation.

DETERMINATION OF THE ATOMIC POSITIONS

After some unsuccessful attempts to solve the structure by means of Harker sections a three-dimensional Pattersson synthesis was calculated on the Hägg-Laurent machine [7]. Most of the maxima in this function were rather broad due to overlapping of several peaks of almost equal height. A method suggested by Lindqvist [8] was used to interpret the Pattersson function.

All atoms of the formula unit $TiCl_4 \cdot POCl_3$ are in the general position 8 (*c*) of space group *P b c a*. Between two crystallographically different atoms there are 8 vectors within the asymmetric unit of the cell, related by the following coordinates for the vectors in Pattersson space.

x_1,y_1,z_1; $\frac{1}{2}-x_1$, $\frac{1}{2}-y_2,z_2$; x_2, $\frac{1}{2}-y_1$, $\frac{1}{2}-z_2$;
$\frac{1}{2}-x_2,y_2$, $\frac{1}{2}-z_1$; x_2,y_2,z_2; $\frac{1}{2}-x_2$, $\frac{1}{2}-y_1,z_1$;
x_1, $\frac{1}{2}-y_2$, $\frac{1}{2}-z_1$; $\frac{1}{2}-x_1$, y_1, $\frac{1}{2}-z_2$.

By combining the maxima in the Pattersson function in groups according to this relation, it proved possible to determine approximate coordinates for seven atoms, Ti, O and 5 Cl.

Using these coordinates, signs were determined for F $(0,k,l,)$, F $(h,0,l,)$ and F $(h,k,0)$. The corresponding Fourier projections were calculated and from these the remaining three atoms could be located. Three successive sets of Fourier projections along all three axes were calculated. From the parameters thus obtained the signs were determined for 550 observed F (h,k,l). This and the following calculations were made on the electronic computer BESK in Stockholm. The atomic scattering factors were evaluated by a two-term expansion of Gaussian functions with constants given by Vand *et al.*[9]

Table 1. Final atomic parameters and their standard deviations.

Atom	x	y	z	$\sigma(x)$ Å	$\sigma(y)$ Å	$\sigma(z)$ Å
Ti	0.0629	0.3616	0.4986	0.005	0.006	0.005
P	0.1875	0.4353	0.2819	0.008	0.009	0.008
O	0.1075	0.4124	0.3564	0.020	0.020	0.016
Cl_1	0.1062	0.5507	0.5424	0.007	0.009	0.007
Cl_2	0.2364	0.3205	0.5231	0.008	0.009	0.008
Cl_3	0.0098	0.2107	0.4306	0.008	0.010	0.008
Cl_4	0.0092	0.3285	0.6506	0.008	0.010	0.007
Cl_5	0.2852	0.5483	0.3130	0.010	0.011	0.011
Cl_6	0.2769	0.3103	0.2522	0.009	0.010	0.008
Cl_7	0.1207	0.4706	0.1548	0.009	0.011	0.008

Two successive three-dimensional Fourier synthesis were carried out, the last one giving a broad and miss-shaped maximum for one of the chlorine atoms, indicating an errouneous assumed position for this atom. All other maxima were sharp and well-defined.

In order to get a better position for this atom signs were determined for F (h,k,l) using the other nine atomic positions. Bounded Fourier projections along the a-axis between the planes $x = 0$ and $x = \frac{1}{2}$ as well as along the c = axis with boundaries $z = 0$ and $z = \frac{1}{2}$ were calculated. These projections gave only one extra well-defined maximum besides maxima at the assumed atomic positions.

At this stage the structure was tested against the three-dimensional Pattersson synthesis. The overlap was very large but all maxima were explained.

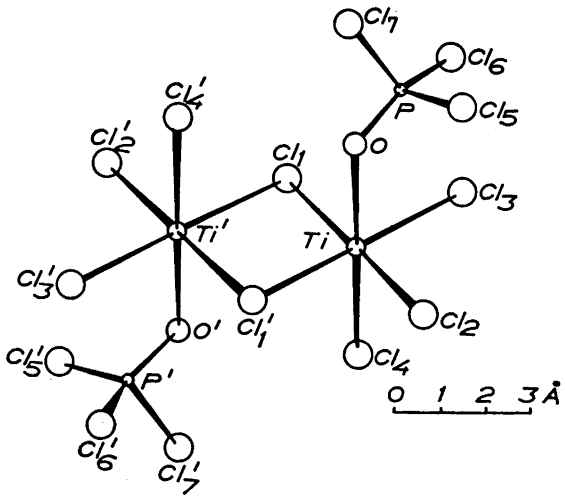

Fig. 1. The molecule of the addition compound $(TiCl_4 \cdot POCl_3)_2$.

REFINEMENT AND ASSESSMENT OF ACCURACY

Two successive three-dimensional Fourier synthesis were computed, in the last one the signs were determined for all F (h,k,l).

Two three-dimensional back-shift corrections were then carried out. To obtain an estimate of the standard deviations in the atomic coordinates Cruickshank's method [10] was used. The second back-shift correction gave smaller shifts than the standard deviation.

The standard deviations obtained with the calculated structure-factors after the back-shift corrections are given in Table 1 together with the final parameters. Using a temperature factor of 4.30 Å^2, the reliability index $R = \Sigma \mid |F_o| - |F_c| \mid / \Sigma |F_o|$ for all observed reflexions is 0.18.

A copy of the observed and calculated F-values can be obtained from this Institute by request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of one adduct molecule is shown in Fig. 1 and the bond lengths and bond angles are given in Table 2 together with their standard deviations.

The molecule is a dimer and the compound should be written $(TiCl_4 \cdot POCl_3)_2$ and named di-μ-chloro-hexachlorobis(phosphorylchloride) dititanium (IV). The double chlorine bridge has not been found earlier in addition compounds of titanium tetrachloride but it has been recognized as a common feature in the adducts of many other acceptor molecules studied by Mann and his school [11]. One example is $(PdBr_2 \cdot Me_3As)_2$. No accurate structure determination has been made of such compounds however.

Table 2. Bond distances and bond angles in $(TiCl_4 \cdot POCl_3)_2$ and their standard deviations.

Distance	(Å)	S.D. (Å)	Angle	(°)	S.D. (°)
Ti — Cl_1	2.44	0.01	Cl_1 — Ti — Cl_1'	78.5	0.3
Ti — Cl_1'	2.54	0.01	Cl_1 — Ti — Cl_3	92.8	0.4
Ti — Cl_2	2.24	0.01	Cl_3 — Ti — Cl_2	98.2	0.4
Ti — Cl_3	2.23	0.01	Cl_2 — Ti — Cl_1'	89.1	0.4
Ti — Cl_4	2.20	0.01	Cl_1' — Ti — Cl_4	91.7	0.4
Ti — O	2.10	0.02	Cl_2 — Ti — Cl_4	96.2	0.4
P — O	1.44	0.02	Cl_3 — Ti — Cl_4	97.4	0.4
P — Cl_5	1.93	0.01	Cl_1 — Ti — Cl_4	92.2	0.4
P — Cl_6	1.98	0.01	Cl_1 — Ti — O	83.0	0.6
P — Cl_7	1.96	0.01	Cl_1' — Ti — O	82.2	0.6
			Cl_2 — Ti — O	87.4	0.6
			Cl_3 — Ti — O	88.1	0.6
			Cl_4 — Ti — O	173.0	0.6
			Cl_3 — Ti — Cl_1'	167.5	0.4
			Cl_2 — Ti — Cl_1	165.0	0.4
			Ti — O — P	151.8	1.3
			O — P — Cl_5	115.6	0.9
			O — P — Cl_6	111.3	0.9
			O — P — Cl_7	111.5	0.9
			Cl_5 — P — Cl_6	107.0	0.6
			Cl_5 — P — Cl_7	106.6	0.6
			Cl_6 — P — Cl_7	104.1	0.5

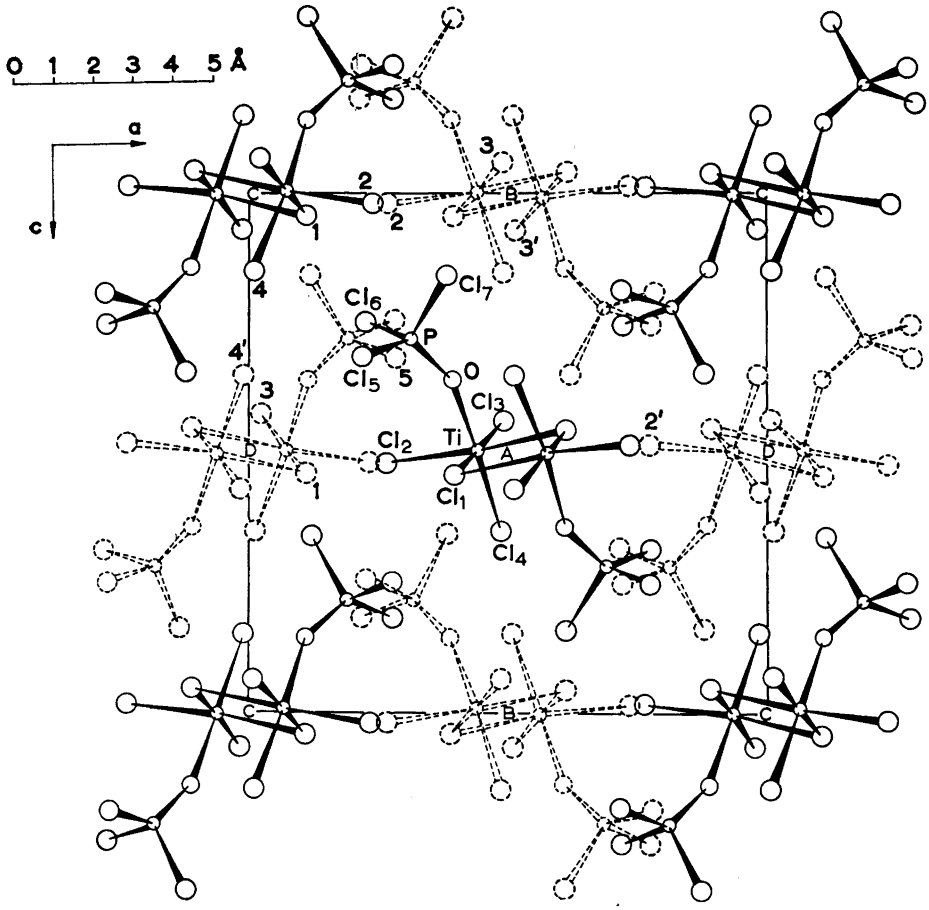

Fig. 2. Projection of the structure along [010], showing different Cl—Cl contacts. The dotted molecules have their centre of symmetry at $y = 1/2$, the other molecules at $y = 0$.

The possible existence of different geometrical isomers in such dimeric molecules was also discussed by Mann and Wells [11]. The present compound has a symmetrical *trans* configuration but the other two modifications found by us may represent other possible geometrical isomers.

The $POCl_3$ molecule has not changed much by the adduct formation and has a structure very similar to free $POCl_3$ [12] and to $POCl_3$ in $SbCl_5 \cdot POCl_3$ [13] (averaged values): P—O 1.44, 1.45 and 1.46 Å; P—Cl 1.96, 1.995 and 1.96 Å; O—P—Cl 112.8°, 114.9° and 112.0°; Cl—P—Cl 105.9°, 103.5° and 106.4°.

The acceptor molecule $TiCl_4$ has changed its co-ordination from tetrahedral to octahedral. The Ti—Cl bond lengths have increased from 2.18 ± 0.04 Å in free $TiCl_4$ [14] to 2.20—2.24 Å ± 0.02 Å for the non-bridging chlorine atoms and the significantly larger values 2.44 and 2.54 ± 0.02 Å for the bridging

Table 3. Packing distances in $(TiCl_4 \cdot POCl_3)_2$.
(*Cf.* Fig. 2.)

	Distance (Å)
$Cl_7(A) - Cl_1$ (C)	3.73
$Cl_7(A) - Cl_2$ (C)	3.66
$Cl_7(A) - Cl_3'$ (B)	3.65
$Cl_6(A) - Cl_1$ (C)	3.65
$Cl_6(A) - Cl_2$ (B)	3.55
$Cl_6(A) - Cl_4'$ (D)	3.63
$Cl_6(A) - Cl_5$ (D)	3.53
$Cl_5(A) - Cl_3$ (D)	3.65
$Cl_5(A) - Cl_4$ (C)	3.72
$Cl_4(A) - Cl_3$ (B)	3.81
$Cl_3(A) - Cl_2'$ (D)	3.48
$Cl_2(A) - Cl_1$ (D)	3.96

chlorine atoms. Such an increase in bond length by bridge formation is to be expected but is easily obscured because of lacking accuracy in the structure determination. Even quite weak bridge interaction is reflected in a bond length increment [15].

The Ti—O bond length of 2.10 Å is almost the same as the Sn—O bond length of 2.12 Å found in $SnCl_4 \cdot 2SeOCl_2$,[16] while the short Ti—Cl bond lengths are appreciably shorter than the corresponding Sn—Cl bond lengths: 2.20—2.24 Å compared with 2.36—2.41 Å. These results will be discussed in a following paper.

Gillespie and Nyholm [17] have suggested that the electronegativity difference between oxygen and the neighbour atoms will determine the bond angle at a bridging oxygen atom. The two known structures of $POCl_3$ addition compounds are in agreement with this idea. Titanium is less electronegative than antimony and the bond angle Ti—O—P is accordingly larger than Sb—O—P: 151.8° compared with 143.7°.

The packing of the molecules is indicated in Fig. 2. All packing distances less than 4.0 Å between different molecules are collected in Table 3.

In the discussion of the structure of another adduct molecule $SeOCl_2 \cdot 2NC_5H_5$[15] it was pointed out that the generally used concepts of covalent and ionic bonds cannot profitably be applied to compounds of this type. A detailed discussion of the conditions will be given in a following paper [18].

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