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CRYSTAL STRUCTURE OF THE COMPLEX $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$

Sir:

In a preceding communication to THIS JOURNAL there was reported[1] the synthesis of a soluble crystallizable complex containing titanium and aluminum showing catalytic activity in the polymerization of ethylene. This fact was taken as supporting our opinion that Ziegler type catalysts are bimetallic complexes. It was also supposed that the two different metal atoms contained in the crystallizable complex were joined by bridges of the same type as the one present for instance in the monochlorodimethylaluminum dimer.[2]

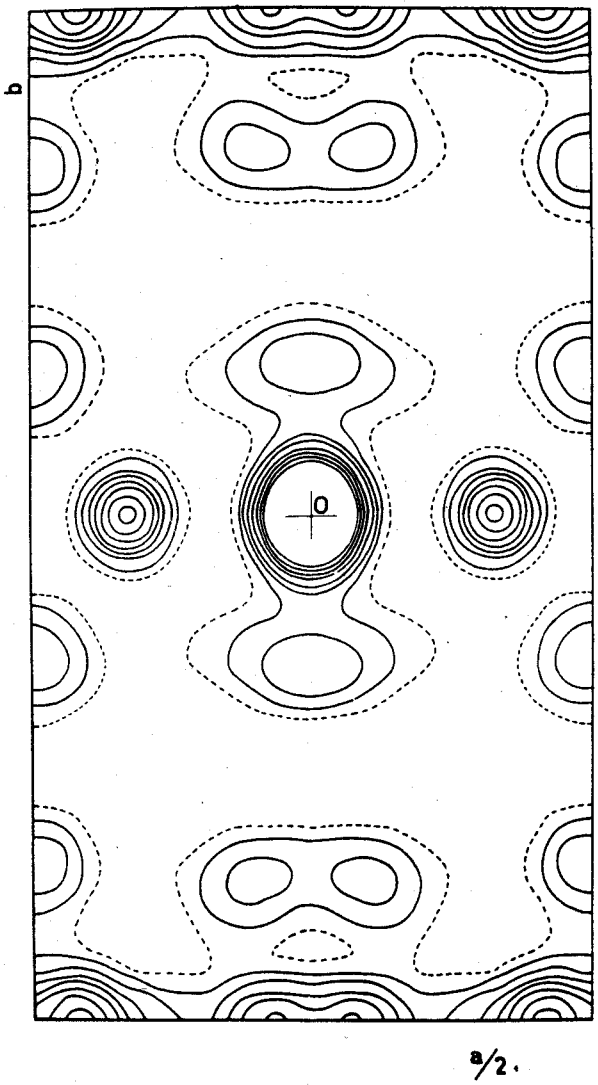

Fig. 1.—Patterson projection on the a-b plane.

To confirm the above reported hypothesis, we wish to communicate some preliminary results of an X-ray examination of single crystals of the complex $(C_5H_5)_2TiCl_2Al(C_2H_5)_2$.

The unit cell constants are

$$a = 15.77 \pm 0.08 \text{ Å}. \quad b = 14.24 \pm 0.07 \quad c = 7.54 \pm 0.04$$
$$\alpha = \beta = \gamma = 90°$$

The number of molecules contained in the unit cell is four, and possible space groups are Pnma or $Pn2_1a$ ($(0kl)$ reflections with $k + l = 2n + 1$ and $(hk0)$ reflections with $h = 2n + 1$ being extinguished).

The space group Pnma requires that the molecule contains a mirror plane. In this case Ti and Al must necessarily lie in this plane ($y = 1/4$).

In fact, the Patterson projection on the a-b plane of the interatomic vectors (Fig. 1) showing a concentration of the highest peaks along the lines $y = 0$ and $y = 1/2$ supports the hypothesis that heavy atoms are contained in the $y = 1/4$ plane.

A complete interpretation of the Patterson projection confirms that: (1) Pnma must be chosen as the correct space group; (2) the position and the weight of the peaks appearing along the lines $y = 0$, $y = 1/2$ may be accounted for by supposing that

$y_{Ti} = y_{ClI} = y_{ClII} = y_{Al} = 1/4$ and $x_{Ti} = x_{ClI} = 0.021$; $x_{ClII} = x_{Al} = 0.183$ or $x_{Ti} = x_{ClII} = 0.271$; $x_{ClII} = x_{Al} = 0.433$

Moreover, (1) from the pseudosystematic absence of the reflections $hk3$ with $h = 2n$ it follows, with other restrictions, that $z_{Ti} - z_{ClI} = z_{ClII} - z_{AlI} \sim 0.333$: (2) a Fourier synthesis (Fig. 2)

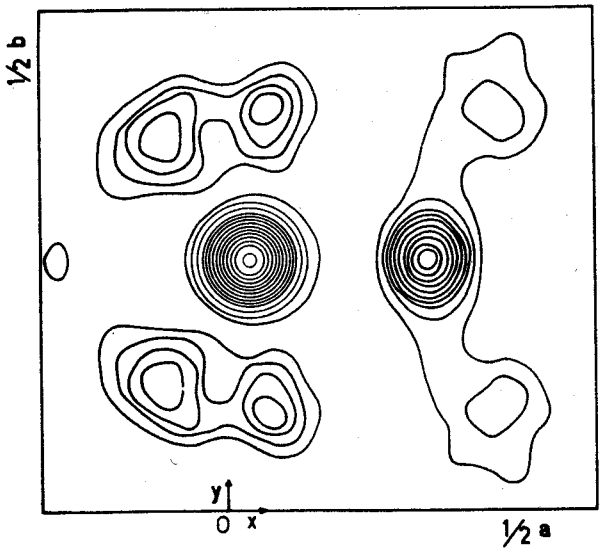

Fig. 2.—Fourier projection on the a-b plane (only half contours of the heavy atoms are drawn).

on the ab plane shows clearly images of the cyclopentadienyl and ethyl groups, which happen to be in suitable positions.

A model of the molecule is shown in Fig. 3.

From the model, we may conclude that: (1) both Ti and Al have a tetrahedral coördination and

(1) G. Natta, P. Pino, G. Mazzanti and U. Giannini, THIS JOURNAL, **79**, 2975 (1957).

(2) G. Natta, P. Pino, G. Mazzanti, and U. Giannini, communication presented at the International Symposium on the Chemistry of Coordination Compounds, Roma, September 15–21, 1957.

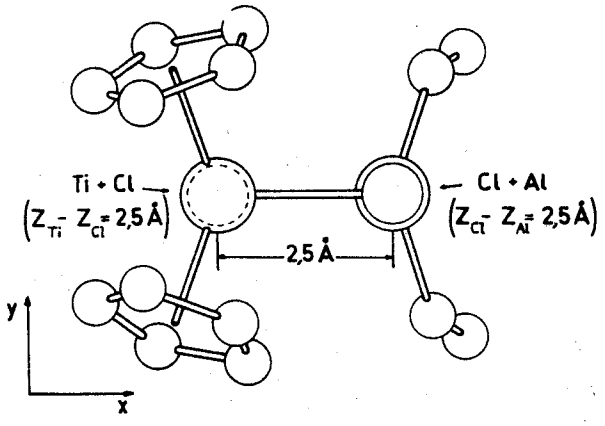

Fig. 3.—Model of the molecule corresponding to the Fourier projection.

are joined by bridges of Cl atoms forming a square ring, the Ti–Cl and Al–Cl distances being about 2.5 Å. (2) The plane of a cyclopentadienyl group is perpendicular to the line joining titanium to the center of the group, the five Ti–C distances being all equal and of the order of 2.3 Å. (3) Ethyl groups are bonded to the Al atoms. The cyclopentadienyl groups in this sandwich $\sigma\pi$-bonded complex are not parallel each other as in ferrocene. The orientation of these groups appears dependent on the type of the hybridization of the metal atom to which they are bonded. Further structural work for this and other similar compounds is going on in our laboratory.

INSTITUTE OF INDUSTRIAL CHEMISTRY
POLYTECHNIC OF MILAN
MILAN, ITALY

GIULIO NATTA
PAOLO CORRADINI
IVANO W. BASSI

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