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The Crystal Structure of Tetraallyldichromium, $Cr_2(C_3H_5)_4$

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A product of the reaction of anhydrous chromium chloride with allylmagnesium chloride in an ether solution was found to be a potential component of a catalyst for the polymerization of olefins. The product can be recrystallized from hydrocarbon solutions in needle-like crystals, brownish-black in color and with a metallic luster. Though this compound is exceedingly inflamable when exposed to air, we have succeeded in determining its chemical composition by elementary analysis and its molecular weight by the cryoscopic method. From the results of infrared absorption, mass spectroscopic analysis, and nuclear magnetic resonance, it was concluded that the compound is tetraallyldichromium, corresponding to the molecular formula $Cr_2(C_3H_5)_4$, and that the reaction can be written as follows:

$$2CrCl_3+6C_3H_5MgCl \rightarrow Cr_2(C_3H_5)_4+C_6H_{10}+6MgCl_2.$$

The yield of the reaction reaches 90—95% if the temperature is controlled properly.

With a hope to look into the mechanism of the catalytic activity, we have undertaken an X-ray crystal analysis of tetraallyldichromium.

Samples sealed in glass capillary tubes filled with argon gas were used throughout the experiment because of their high sensitivity to air. The single crystals used were prisms elongated along the c-axis, with dimensions of (0.1—0.2)×(0.1—0.2)×(1.5—3.0)mm. The crystal data are as follows: the molecular weight is 268; the unit cell is tetragonal with $a=18.19\pm0.09$, $c=7.50\pm0.05$ Å, and contains eight molecules of $Cr_2(C_3H_5)_4$; the space group is $P\bar{4}2_1c$—D^4_{2d}; the density calculated is 1.44 $g\cdot cm^{-3}$.

X-Ray intensities were visually estimated from multiple-film equi-inclination Weissenberg photographs taken from the zeroth to the fifth layer around the c-axis with Ni-filtered Cu*Ka* radiation. Five oscillation photographs taken using the equi-inclination method were prepared in order to find the scale factors by comparing the structure factors of reflections appearing in each layer with those of the equatorial reflections. The relative intensities of all the six layer reflections put on the same scale were corrected for the Lorentz-polarization factor,

Table 1. The final atomic positions

	X/a	*Y/b*	*Z/c*
Cr1	0.2113	0.0524	0.1791
Cr2	0.2819	−0.0290	0.1519
C11	0.3708	0.0294	0.0274
C12	0.3342	0.0923	0.1400
C13	0.2732	0.1377	0.0463
C21	0.2108	0.0955	0.4631
C22	0.1590	0.0452	0.4578
C23	0.1060	0.0351	0.3156
C31	0.1494	0.0267	−0.0600
C32	0.2158	−0.0017	−0.1250
C33	0.2413	−0.0736	−0.0980
C41	0.2616	−0.1439	0.2552
C42	0.2767	−0.0979	0.4104
C43	0.3391	−0.0485	0.4126

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† Deceased 31 May, 1967.

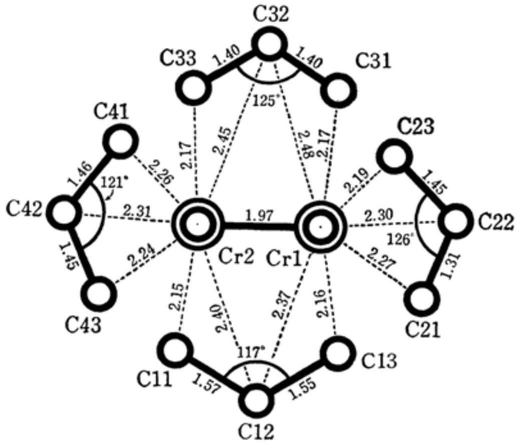

Fig. 1. Interatomic distances (Å) and bond angles (°).

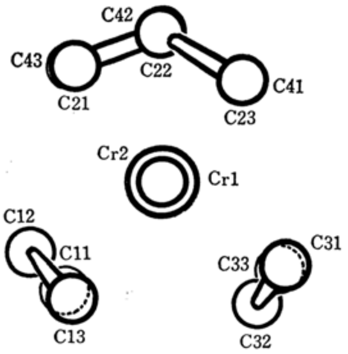

Fig. 2(a). The configuration of the complex, Cr_2-(C_3H_4), viewed along the Cr—Cr axis.

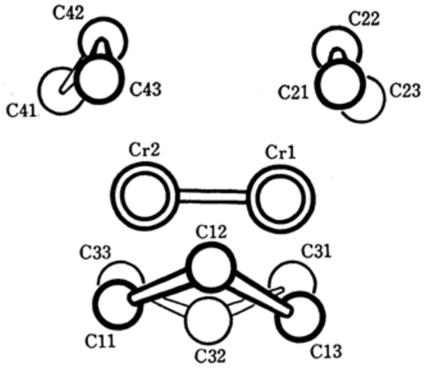

Fig. 2(b). The configuration of the complex, $Cr_2(C_3H_5)_4$, viewed along an axis perpendicular to the Cr–Cr.

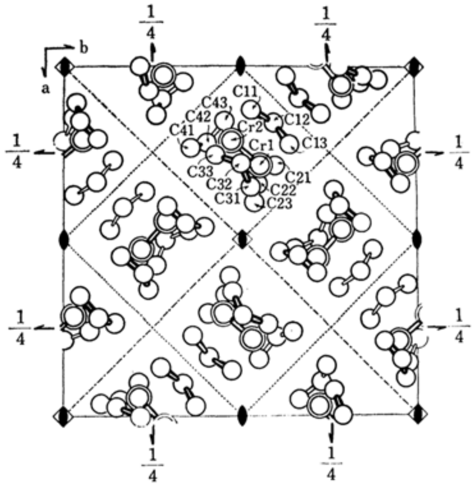

Fig. 3. The packing arrangement of the complex, $Cr_2(C_3H_5)_4$, viewed along the c-axis.

but not for the absorption effect. The relative values of the observed structure factors of 656 independent reflections were converted into an absolute scale by Wilson's method.

The positions of the chromium atoms were determined from a three dimensional Patterson function and refined by the least-squares method. Twelve carbon atoms were found on a Fourier map calculated using the phases of the heavy atoms alone. The fourteen positions thus obtained were refined by the least-squares method, taking into consideration the anisotropic thermal motions of all the atoms and the anomalous dispersion effect of chromium. The final R factor was 11.2%.

The atomic positions thus obtained are given in Table 1; the estimated maximum deviations are 0.06 Å for the carbon and 0.006 Å for the chromium atoms. The interatomic distances and bond angles are shown in Fig. 1. The configuration of the complex, $Cr_2(C_3H_5)_4$, and the packing arrangement in the unit cell are shown in Figs. 2 and 3 respectively. Four allyl ligands make a distorted tetrahedron around the two directly-coupled metal atoms. The Cr–Cr distance, 1.97Å, in the molecule is considerably smaller than that found in metallic chromium, 2.50 Å; it is indeed, the smallest metal-to-metal distance reported so far for organometallic compounds. The four ligands may be divided into two groups on the basis of the mode of coordination. The planes of the C11–C12–C13 and C31–C32–C33 groups are nearly parallel to the Cr–Cr axis and each of these groups is coordinated to both of the chromium atoms. On the other hand, the C21–C22–C23 and C41–C42–C43 groups are approximately perpendicular to the Cr–Cr axis and each is coordinated to one of the chromium atoms. The average bond length of the C–C bond is 1.45 Å, which is comparable with the mean value of the single and double bonds of the carbon atoms. None of the intermolecular interatomic distances are abnormally short, so the molecules are held together by the van der Waals interactions alone.

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