THE TWINNING IN CARBONYL PYRAZINE *BIS* (TRIPHENYL ARSINE) RHODIUM (1) PERCHLORATE $[Rh(CO)(Pyz)(Ph_3As)_2]ClO_4$

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ABSTRACT

The measured cell constants, the observed extinctions of the reflections and the double spots in the Weissenberg photographs, all indicate the 'pseudo-symmetry twinning' in carbonyl pyrazine *bis* (triphenyl arsine) rhodium (1) perchlorate crystals.

INTRODUCTION

THE synthesis of a number of cationic complexes of rhodium(1) has been reported. Carbonyl pyrazine *bis* triphenyl arsine) rhodium(1) perchlorate crystals have been obtained by the reaction of the complex $[Rh(CO)_2(Ph_3As)_3]ClO_4$ with the ligand pyrazine in alcohol (Reddy and Ramesh, 1974[1]).

X-ray study of these crystals were undertaken to collect the preliminary data and the intensity data needed for crystal structure analysis. Because the crystals exhibited twinning, further work on structural analysis was not continued.

During the alignment of the crystals about the crystallographic axes other than the needle axis (*b*-axis), slight deviation from the rotation axes showed considerable distortion of the layer line spots. A number of investigators have attributed that this may be due to twinning in the crystal. In the twinned crystals we have more than a single individual of the same substance. The individuals are so blended that their appearance at first sight is that of a single individual crystal (Tutton, 1922[2]). There are, different types of twinning. The pseudo-merohedral symmetry in crystals of para-red (Grainger and McConnel, 1969[3]), the pseudo-symmetry twinning in 5, 5'-bilsoxasole crystals (Cannas, Carta and Marongiu, 1972[4]), the study of the twinned felspars (Ito and Sadanaga, 1952[5]) may be quoted as examples. It is well known that double spots appear in the diffraction pattern due to twin structure. Each reciprocal lattice point, due to one individual of the twin may either coincide or almost coincide with the reciprocal lattice point belonging to the other individual (Cannas, Carta and Marongiu, 1972[4]). The pseudo-symmetry twinning observed in carbonyl pyrazine *bis* (triphenyl arsine) rhodium(1) perchlorate has been reported in this article.

EXPERIMENTAL

The unit cell dimensions of the above crystals were determined using rotation as well as zero layer Weissenberg pictures taken about different crystallographic axes. Copper K_α radiation was used. The crystal lattice is triclinic with cell constats

$$a = 18{\cdot}94\ \text{Å}, \quad \alpha = 90°.$$
$$b = 10{\cdot}31\ \text{Å}, \quad \beta = 70°\ 16'.$$
$$c = 20{\cdot}54\ \text{Å}, \quad \gamma = 86°\ 59'.$$

The number of formula units is two per unit cell. The molecular weight of the compound is 922·83 and its linear absorption coefficient is 66·73 cm^{-1}. The calculated and the measured densities are $d_c = 1{\cdot}57$ gm cm^{-3} and $d_m = 1{\cdot}56$ gm cm^{-3} respectively. The crystal density was measured by floatation technique using carbon tetrachloride and bromobenzene. The measured density and the calculated density are in good agreement indicating two formula units in a cell.

DISCUSSION

Based on cell constants, the crystal lattice is triclinic. But the extinctions observed (*hol*, $l = 2n + 1$) indicate that it belongs to pseudo-monoclinic space group Pc with one of the angles equal to 90°, the other being close to 90°. The cell constants of the crystal, the extinction of the reflections and the double spots in the Weissenberg photographs, all indicate the pseudo-symmetry twinning.

The Weissenberg pictures taken about the needle axis showed no splitting of spots. The zero and the first layer Weissenberg pictures are shown in Fig. 1. The absence of (*hol*) reflections for $l = 2n + 1$ confirms that $c = 20{\cdot}54$ Å which otherwise should be equal to half this value. The zero and the upper layer pictures taken about the other two axes showed splitting of spots. Only the zero and the first layer Weissenberg pictures taken about the *a*-axis are shown in Fig. 2. The Weissenberg pictures taken about the *c*-axis were not good for reproducibility and are not given here.

Regarding the Weissenberg pictures taken about the needle axis, no splitting of spots was observed. This may be due to the fact that the reciprocal lattice point of one individual crystal is coincident with that of the other individual of the twin. With respect to the Weissenberg pictures taken

about the other two axes, the reciprocal lattice of the two individuals of the twinned crystal is non-coincident and gives rise to double spots. It may be concluded that the two individuals of the twinned crystals are formed from independent nuclei during the process of crystallization.

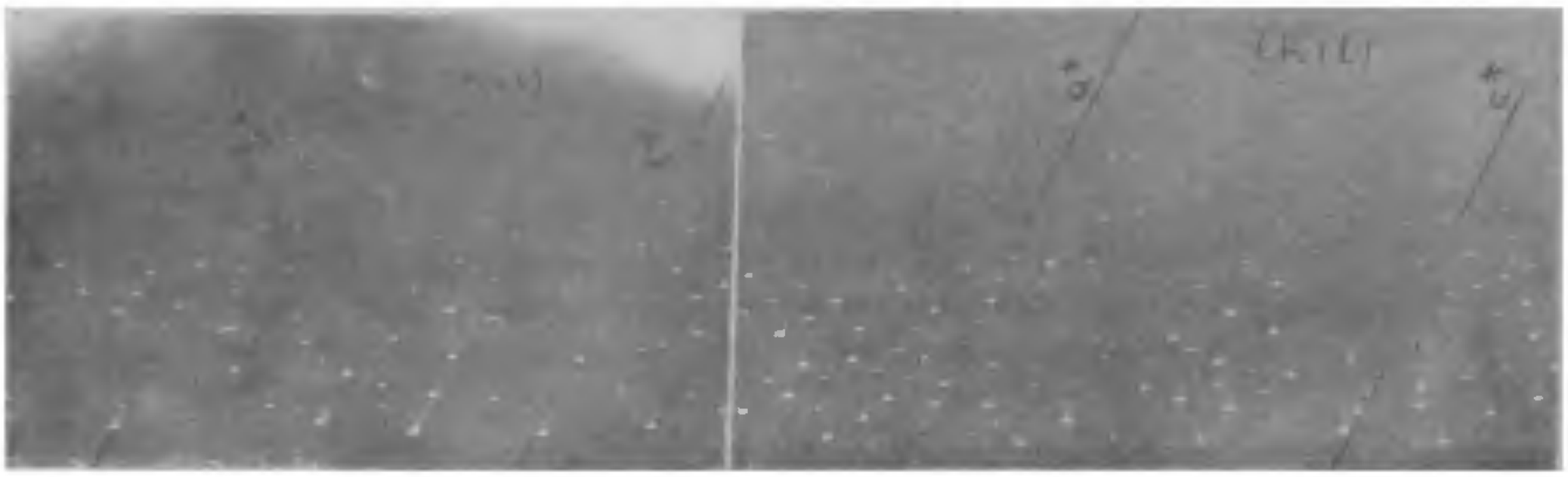

FIG. 1. *hol* and *hll* Weissenberg pictures no splitting of spots.

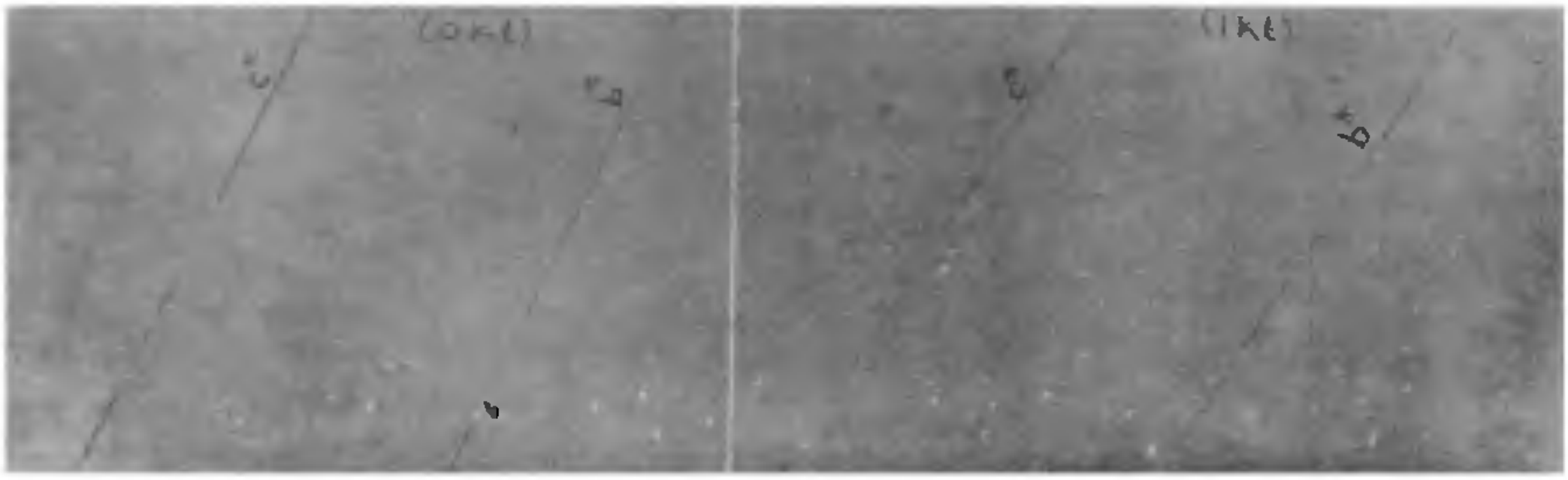

FIG. 2. *okl* and *1kl* Weissenberg pictures showing splitting of spots.

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STUDIES ON THE TOTAL SYNTHESIS OF 3-DEOXY-7-OXAESTRONE: SYNTHESIS OF 1-DIETHYLAMINO-4-BENZYLOXYBUT-2-YNE AND 1-DIETHYLAMINO-4-BENZYLOXYBUT-2-ENE

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WITH a view to synthesizing the hitherto unknown[1] 3-deoxy-7-oxaestrone (I), the required starting material, 3-benzyloxy-1-propyne[2] (II), was prepared either by treating the sodio-derivative of benzyl alcohol with propargyl bromide or the sodio-derivative of propargyl alcohol with benzyl chloride in refluxing propargyl alcohol. Initially conversion of (II) into the desired Mannich base, 1-diethylamino-4-benzyloxybut-2-yne(III), was attempted adopting strictly the conditions reported by Hughes and Smith[3,4] but the Mannich base(III) was obtained only in low yield (15%). A 46% yield of the desired Mannich base(III) was, however, achieved by treating (II) with a mixture of