

The equilibrium constant  $K$  in numerous cases largely favours the 17-normal-compound; since the decrease of free energy is given by  $-\Delta F^0 = RT \ln K$ , this is the thermodynamically stable isomeride, so that, independently of the mechanisms of the processes involved, the net effect of all factors operating is to favour  $\beta$ -orientation of the acetyl group. An analogous argument can be adduced for the case of a 17-carbomethoxy group. The equilibrium ( $J$ ) is thus related to reactions  $A, B, C, D$  inasmuch as  $C_{17}$  is directly involved, but conforms to the reactions  $E, F, G, H$  because the acetyl group lies outside the range of the effects, discussed above, due to steric hindrance and asymmetric induction; it shows that the 17 $\beta$ -acetyl group is more attracted or, conversely, that the 17 $\alpha$ -acetyl group is more repelled, by other groups, although the source of such attraction or repulsion is obscure.

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- <sup>1</sup> Cf. Fieser, L. F., and Fieser, M., "Natural Products Related to Phenanthrene", 410, 411 (3rd edit. New York: Reinhold, 1949).  
<sup>2</sup> Dostrovsky, Ingold and Hughes, *J. Chem. Soc.*, 173 (1946).  
<sup>3</sup> Whitmore and Rothrock, *J. Amer. Chem. Soc.*, 54, 343 (1932).  
<sup>4</sup> Quayle and Norton, *J. Amer. Chem. Soc.*, 62, 1170 (1940).

### Structure of *Trans*-Potassium Dioxalato-Diaquo-Chromiate

THE crystals of *trans*-potassium dioxalato-diaquo-chromiate,  $K[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ , are dark red in colour, very hard, and show a very pronounced tendency to intergrow. They are monoclinic, and from X-ray measurements the size of the unit cell was determined as:

$$a = 7.85 \text{ \AA}, b = 5.72 \text{ \AA}, c = 13.88 \text{ \AA}, \beta = 109^\circ 30'$$

The density of the compound is 2.02 gm./c.c. The unit cell contains two of the above formula units, and the space group is  $P2_1/c$  ( $C_2^2h$ ).

For an accurate determination of the structure the method of double Fourier series was used. Fig. 1 shows a projection of the structure on the  $ac$ -plane when viewed parallel to  $b$ . A second projection on the  $bc$ -plane made it possible to assign co-ordinates to all the atoms. Fig. 2 shows the dimensions of the  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$  complex ion. The two water molecules, marked  $\text{H}_2\text{O}$  (1), in this complex ion are at distances 2.02 Å from the chromium atom. The line joining them is perpendicular to the plane in which the two oxalato groups of the complex ion is found to lie. The dimensions in Fig. 2 can be compared

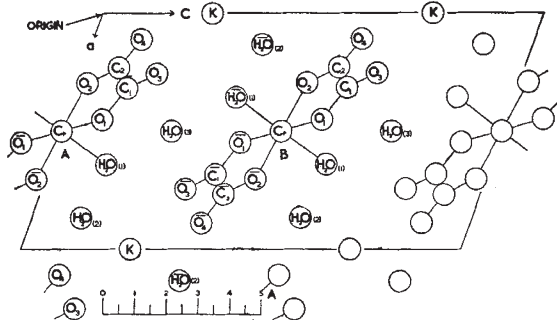


Fig. 1. Projection of the structure in direction  $b$  on the  $ac$ -plane. A formula unit marked  $B$  is derived from one marked  $A$  by the operation of a glide plane parallel to (010)

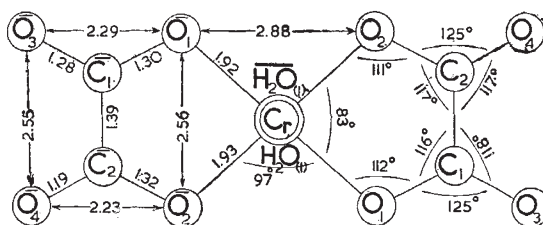


Fig. 2. The complex ion  $[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$

with those found by Zachariasen<sup>1</sup> and by Robertson and Woodward<sup>2</sup> for oxalic acid dihydrate.

The packing of the complex ions in the structure is such that the plane of the two oxalato groups in each complex ion is inclined at an angle of  $61^\circ$  to the  $ac$ -plane, while the long axis of a planar  $\text{Cr}(\text{C}_2\text{O}_4)_2$  group makes an angle of about  $9^\circ$  with the  $ac$ -plane. Each potassium ion is surrounded by eight oxygen atoms, six of these oxygens approaching a potassium ion to within a distance of 2.74 Å, the other two approaching it to within a distance of 3.10 Å. The eight oxygens surrounding a potassium ion are parts of four different formula units, and these units all lie in approximately the same plane as the potassium ion. If we consider formula units of the type marked  $A$  and  $B$  (Fig. 1) to form an approximate layer-like structure, then it seems likely that the binding forces within such layers are mainly due to ionic bonds between potassium and complex ions. The water molecules not belonging to the complex ions, and marked  $\text{H}_2\text{O}$  (2) and  $\text{H}_2\text{O}$  (3) in Fig. 1, form zig-zag chains of length 2.66 Å, running through the structure from one layer to the other, so that hydrogen bonding appears to be largely responsible for the binding forces between such layers.

A detailed description of this work will be published elsewhere.

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<sup>1</sup> Zachariasen, *Z. Krist.*, 89, 422 (1934).

<sup>2</sup> Robertson and Woodward, *J. Chem. Soc.*, 1817 (1936).

### Reactions of 9-Anthraldehyde in Sunlight

THE investigations recently reported<sup>1</sup> have been continued, and I wish to put the following facts on record. The photo-experiments mentioned below have been carried out in a sealed 'Monax' or 'Pyrex' glass tube (Schlenk tube) in an atmosphere of dry carbon dioxide; in all cases the dark experiments were negative.

(a) A number of photo-reactions between phenanthraquinone and aromatic aldehydes has been described<sup>1</sup>. A similar reaction has been carried out between 9-anthraldehyde and phenanthraquinone, retenequinone and chrysoquinone respectively, affording 9-anthrylhydroxymethylene ether of 9:10-dihydroxyphenanthrene (I), melting point  $228^\circ$  from xylene (found: C, 84.1; H, 4.3;  $M$  (micro-Rast), 401.  $\text{C}_{22}\text{H}_{18}\text{O}_3$  requires C, 84.1; H, 4.3 per cent;  $M$ , 414), 9-anthrylhydroxymethylene ether of 9:10-