Chemistry. — "*On the Pseudo-symmetry of Racemic Potassium Chloro-sulfoacetate.*" By Prof. F. M. JAEGER.

(Communicated at the meeting of May 30, 1925).

The crystalform of racemic *potassium-chloro-sulfoacetate*, whose constitution is: $\left\{\begin{matrix} \mathrm{CHCl\,.\,SO_3K} \\ | \\ \mathrm{COOK} \end{matrix}\right\}_2 + 3\,H_2O$, has not been well known up till now. RATHKE [1]) concluded from his measurements that the compound must be considered to be tetragonal, while DOELTER [2]) described the substance as possessing rhombic symmetry, as a result of very insufficient data obtained by him with evidently badly developed crystals. These showed a combination of a rhombic bipyramid $\{111\}$ and the basis $\{001\}$; the angle $(1\bar{1}1):(111)$ was found to have values ranging from 85° to 88°, while for the angle $(001):(111)$ values are given oscillating between 68° and 72°.

Prof. BACKER was so kind as to put at my disposal some crystals, which he obtained by slow evaporation from aqueous solutions containing also *potassium bromide*. These beautiful crystals appeared to be perfectly clear and to possess perfectly plane, lustrous faces; moreover they showed optical properties of a very particular character, which invited to closer examination. The results obtained during this investigation are here recorded.

The salt crystallizes most frequently in the shape of thin square plates and sometimes also as thick quadratic crystals which are truncated at two opposite corners (Fig. 1). The faces of these crystals were in all cases highly lustrous; the angular values in separate individuals appeared to be very constant, accurate measurements being therefore possible here.

The symmetry is apparently rhombic-bipyramidal, with a very close approximation to tetragonal symmetry; the geometrical form may, therefore, be safely described as pseudo-tetragonal. This fact, which finds its expression also in the values of the crystal-parameters:

$$a : b : c = 0.9973 : 1 : 2,7650$$

explains at the same time the discordant results of the measurements of the earlier observers mentioned above.

Observed forms: $c = \{001\}$, always strongly predominant and highly lustrous; on microscopical observation the faces of this form show a very fine striation parallel to the edge $(001):(101)$.

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[1]) B. RATHKE, Lieb. Ann. der Chemie, **161**, 166, (1872).

[2]) C. DOELTER, Sitzber. d. Akad. d. Wiss. Wien, **93**, II, 685, (1886); Monatshefte **7**, 159.

Moreover: $\omega = \{111\}$ and $o = \{113\}$, both sometimes equally broad, but in most cases ω appreciably broader than o; the planes of ω give also much better reflections than o, the faces of this latter form being usually finely striated parallel to the edge (001) : (111). The bigger and thicker individuals show, moreover, the form $r = \{101\}$, which has also very lustrous faces, yielding very sharp reflexion-images. The plane angles on $\{001\}$ are 89°48′, resp. 90°12′; the faces of $\{001\}$ and in the same way the opposite faces of $\{113\}$ are never completely parallel, but deviate from parallel orientation about 10′.

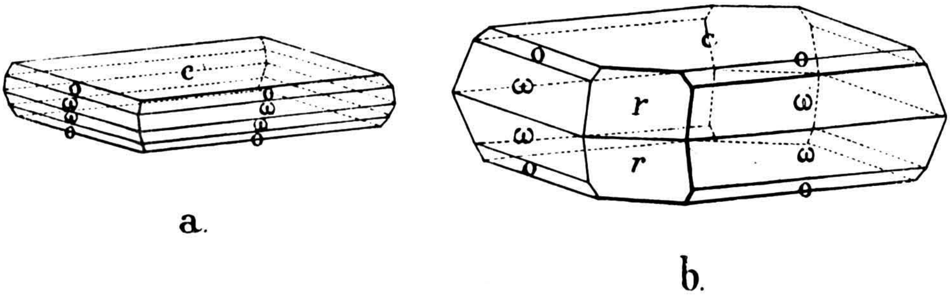

Fig. 1.

Doubtlessly this fact is connected with the rather complicated structure of the crystals explained in the following.

Angular Values:	*Observed:*		*Calculated:*	
$c : \omega = (001) : (111) =$*	75°	40½′	—	
$c : r = (001) : (101) =$*	70	10½	—	
$c : o = (001) : (113) =$	52	34	52°	33′
$o : \omega = (113) : (111) =$	23	6½	23	7½
$\omega : \omega = (111) : (11\bar{1}) =$	28	39	28	39
$o : o = (113 : (\bar{1}13) =$	68	36	68	26
$\omega : \omega = (111) : (1\bar{1}1) =$	86	37	86	18
$\omega : \omega = (111) : (\bar{1}11) =$	86	21	86	41
$o : o = (113) : (1\bar{1}3) =$	68	25	68	10
$r : r = (101) : (10\bar{1}) =$	39	39	39	39

The crystals show a good cleavage parallel to $\{001\}$.

Optical Properties.

In parallel polarized light the crystals show diagonal extinction on $\{001\}$. However, they clearly possess a zonal structure: generally there is a central, quadratically limited field, which is divided into four quadrants separated by boundary-lines parallel and perpendicular to the edge $c:r$. The pairs of opposed quadrants have always the same optical orientation. Round this central part succesive zones are arranged,

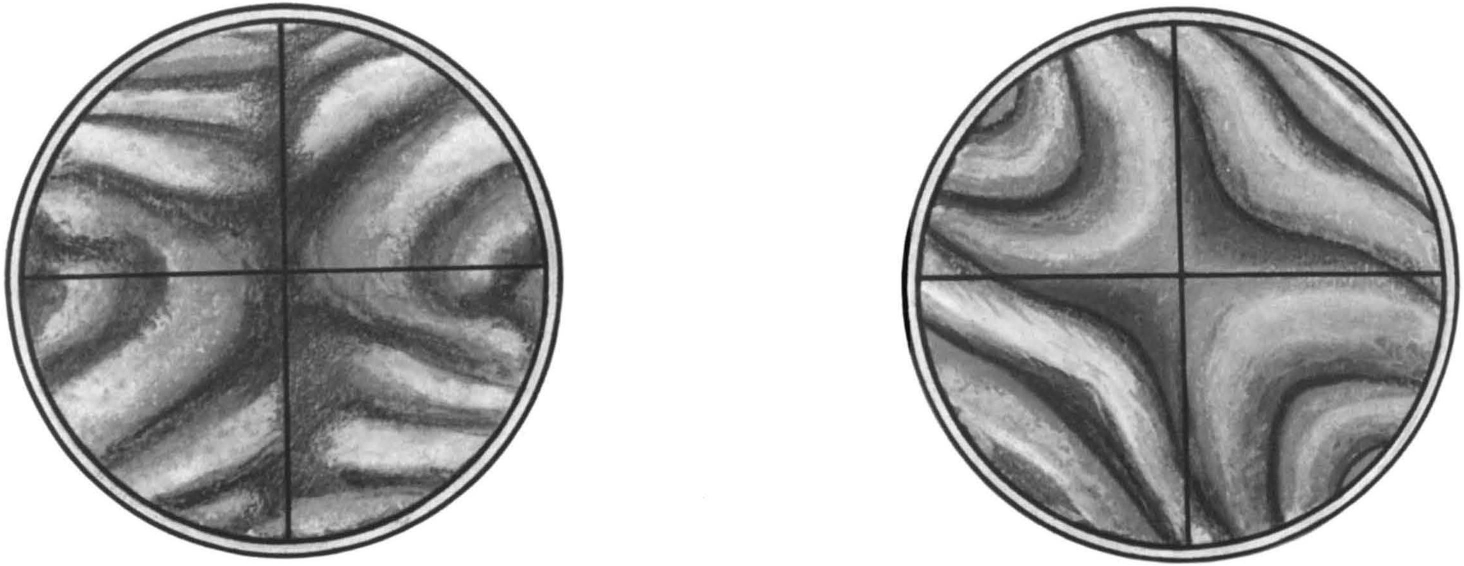

Fig. 2

a.
Normal Position
(Axial plane horizontally orientated)

b.
Diagonal Position

RACEMIC POTASSIUM-CHLOROSULFOACETATE

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which go parallel to the boundaries of the square plates; these zonal bands appear to get thinner, as they approach the circumference of the crystal-plates. The plane of the optical axis for yellow light in each band is parallel to {100}; the direction of the *c*-axis is that of the first bisector, with negative optical character.

In convergent polarized light one observes a strangely shaped interference-image (Fig 2[a]), if the principal sections of the Nicol's prism are parallel to the diagonals of (001). When the crystal is turned over 45°, the interference-image is that represented in Fig. 2[b]; there are no branches of a dark hyperbola present. The axial image of Fig. 2[a] is evidently only *centrically*-symmetrical: it shows an extremely strong *crossed* dispersion of monoclinic character, with $\varrho < v$.

From this it follows that the structure is only rhombic in appearance; in reality it is monoclinic. By an almost perpendicular crossing of monoclinic lamellae a polysynthetic twin-structure is created, which very closely imitates a pseudo-rhombic, and almost tetragonal regularity. To this intergrowth of monoclinic lamellae correspond as well the fine striations on the faces of {001} and {113}, as the irregularities of the architecture of the crystals, as they are revealed by the more significant oscillations of the angular values in the zone of the edge (001) : (101) caused by the want of parallelism between (001) and $(00\bar{1})$. It was impossible to intensify the lamellar appearance of the crystals by heating, because the crystals on heating very soon show numerous bursts and then get turbid and opaque by deshydration.

The pseudo-symmetrical character of the crystals thus being established beyond all doubt, suspicion arises that the salt is no racemate in the proper sense of the word, but rather a pseudo-racemic intergrowth of 50 % of the right- and lefthanded antipodes. Certainty about this could only be obtained, if it were possible to compare the crystalforms of the optically active components separately with that of the salt described. However, this experiment remains irrealisable as a consequence of the fact that the potassium-salts of the optically-active chloro-sulfoacetic acids are very rapidly racemized in solution, it being, therefore, impossible to get measurable crystals of both components in a pure state.

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