Chemistry. — *"Investigations on* Pasteur's *Principle concerning the Relation between Molecular and Crystallonomical Dissymmetry:* **VI.** *On the Fission of Potassium-Rhodium-Malonate into Its Optically-active Components."* By Prof. F. M. Jaeger and William Thomas. B. Sc.

(Communicated in the meeting of June 29, 1918).

1. Some time ago one of us[1]) described the crystalform of *racemic Potassium-Rhodium-Malonate*: $K_3\{Rho(C_3H_2O_4)_3\} + 3H_2O$, and hinted at the possibility of separating this salt into its optically-active components. In the following we are now able to describe the results of the respective experiments, which have led to a positive result, and to give a review of the highly remarkable rotation-dispersion of these new salts.

The racemic salt nesessary for these experiments was prepared in the following way. A 3 °/₀-solution of pure $Na_3RhoCl_6 + 9H_2O$ was heated to 40° C, and then precipitated by means of a 10 °/₀ solution of caustic potash, so much of the base being added, that the liquid showed a feeble alkaline reaction. The precipitate is separated from the excess of potash as well as possible by repeated decantation in high cylindrical vessels; it settles down extremely slowly, so that this operation takes much time. Then the precipitate is brought into a round bottom distilling-flask and heated under a reflux-cooler some forty hours with a solution of the calculated amount of *potassium-bimalonate*: $KHC_3H_2O_4$, and some free *malonic acid*, until the precipitate no longer diminishes in quantity. The red coloured liquid is then filtered, and concentrated on the water-bath: on slow evaporation at room-temperature there soon appear red flat crystals of the complex malonate, which are once more recrystallised from water for purification. The residue in the flask is again changed into the complex *sodium-rhodium-chloride*: $Na_3RhoCl_6 + 9H_2O$ in the usual way, and afterwards precipitated as described in the above.

§ 2. After a series of attempts we succeeded in separating this salt, which crystallises in beautiful monoclinic crystals[2]), into its optically-active components by the aid of its *cinchonine*-salt.

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1) F. M. Jaeger, Proceed. Kon. Acad. Amsterdam, **20**. 276. (1917).
2) *loco citato*, p. 277.

For this purpose the *potassium*salt is first converted into the *barium*salt, by adding a strong solution of 3 molecules of *barium= chloride* to a concentrated solution of 2 molecules of the potassium-salt: a yellow precipitate is formed, which dissolves rather easily in hot water, but which can be almost completely precipitated from its aqueous solution by the addition of 97 % alcohol. This barium-salt was now dissolved in water at 50° C, and then a solution of one equivalent *cinchonine-sulphate* [1]), also heated to 50° C, was added to it. The solutions need not be too concentrated, because the *cinchonine-rhodium-malonate* will otherwise partly precipitate, as it is only sparingly soluble. The bariumsulphate formed is carefully sucked off, and by washing with water of 45° C. all the included yellow *cinchonine*-salt eliminated. On standing for 24 hours in a large crystallising-dish, the liquid begins to deposit beautiful, pale yellow and often in rosettes united needles of the *cinchonine*-salt of the *laevogyrate* component, as will soon be shown. On repeated partial evaporation of the mother-liquid on the waterbath, the successive fractions were separately collected and investigated. The first three fractions appeared to contain the *left*handed component; the fourth fraction gave the almost pure *dextrogyrate* antipode, the fifth and sixth fractions the pure dextrogyrate component immediately. It is a remarkable fact that the *cinchonine-l-malonate* and the *cinchonine-d-malonate* are both *dextro*-gyratory, notwithstanding the very large rotation of opposite sign of the complex ions present therein. This peculiar behaviour was checked by us by a special control, namely by preparing the free *potassium*-salts again from the *cinchonine*-salts used in the polarimetric measurements. We could easily prove in this way, that the salts thus obtained, really represented the right and left antipodes. From the pure *laevogyrate potassium*salt we once more prepared the corresponding *cinchonine*-salt by means of the *barium*-salt; the rotations determined with this especially prepared salt proved to be positive, and they agreed very well with those formerly found. We have also investigated the influence of the addition of three molecules of *cinchonine* to a solution of the optically-active *potassium*-salts, and the rotations found with these solutions were compared with those

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[1]) Originally we tried to reach our purpose by means of the *strychnine*-salt, as in the case of the *rhodium-oxalate*. However, these experiments had no result, the *potassium*salt prepared from the carefully fractionated *strychnine*-salt by *potassium-iodide* being always optically-*inactive*. It is difficult to say whether racemisation or partial racemism is the cause of this; but only after several failures we passed to the use of *cinchonine*.

of *cinchonine* itself: the observed rotations appeared to be practically identical with those of the *cinchonine-l-rhodium-malonate*, so that evidently the influence of the three molecules of *cinchonine* far outweighs that of the laevogyrate *rhodium-malonate-ion* itself.

The last fractions of the crystallisation-series of the *cinchonine*-salt finally gave pure *cinchonine*, a small amount of the dextrogyrate salt and a certain quantity of the racemic salt remaining in the last mother-liquids. Evidently also here the repeated evaporation on the waterbath, just as in the case of the corresponding *oxalate*, seems to cause a partial hydrolysis. Analysis taught us that the *cinchonine-d-rhodium-malonate* crystallises with $3\,H_2O$; the corresponding *cinchonine-l-rhodium-malonate* with $\frac{1}{2}\,H_2O$. This last mentioned salt could not be heated above 100° C, being less stable than the right-handed salt, it is rapidly decomposed with formation of a dirty brown powder.

For the rotation-dispersion of the *cinchonine*-salts we found the following values:

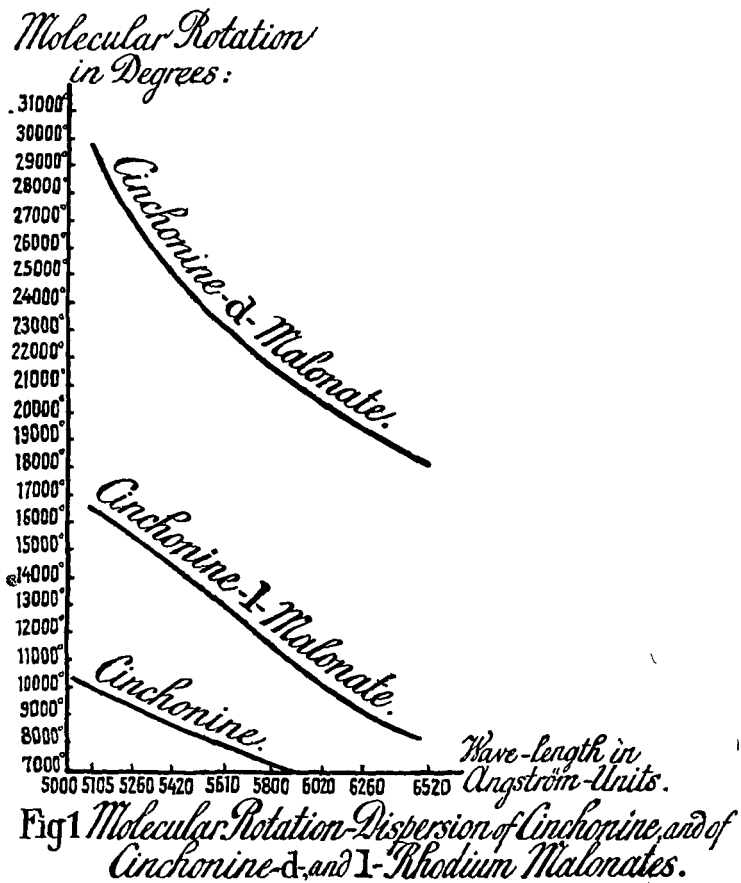| I. Cinchonine-*d*-rhodium-malonate ($+$ 3 H₂O).		
Wave-length in A. U.:	Observed Rotation in Degrees:	Molecular Rotation in Degrees:
5105	+ 1,37°	+ 30010°
5260	1,23	26943
5420	1,14	24972
5610	1,07	23406
5800	0,99	21686
6020	0,94	20591
6260	0,88	19277
6520	0,84	18400

The solution investigated contained 0,3070 grams of the hydrated salt in 100 grams of the liquid.

The results obtained are plotted in the figure 1. It shows us, that *both* curves are situated *above* that of pure *cinchonine*, notwithstanding the fact, that one of them contains the strongly negatively rotating complex *rhodium-malonate*-ion; of a simple superposition of the optical activities there is therefore no question.

The transformation of the *cinchonine*-salts into the corresponding *potassium*-salts was carried out in the following way. The pure

II. Cinchonine-*l*-rhodium-malonate ($+ \frac{1}{2} H_2O$).		
Wave-length in A.-U..	Observed Rotation in Degrees:	Molecular Rotation in Degrees.
5105	$+ 0{,}65$	$+ 16647°$
5260	0,61	15622
5420	0,57	14598
5610	0,52	13384
5800	0,45	11525
6020	0,40	10244
6260	0,36	9220
6520	0,32	8195

The solution used had 0,2538 grams of the hydrated salt in 100 grams of the liquid.

Fig. 1 *Molecular Rotation-Dispersion of Cinchonine, and of Cinchonine-*d*, and *l*-Rhodium Malonates.*

cinchonine-salt is ground with about ten times its weight of potassium-iodide, and a small amount of water added to the finely pulverized mass. The mixture is allowed to stand for 24 hours at room-temperature; the yellow liquid is then sucked off as sharply as possible from the precipitate The reddish yellow filtrate is precipitated by 97 °/$_0$-alcohol, and the pale yellow precipitate of *potassium-rhodium-malonate* thus formed recrystallised from a little water. During the evaporations on the waterbath a noticeable racemisation does not occur. It is advisable to add as little water as possible during the transformation of the *cinchonine*-salt by means of potassium-iodide, as otherwise the precipitation with alcohol is very incomplete.

3. The optically-active components are, like the racemic salt, but in yet higher degree, very soluble; at ordinary temperatures the racemic form is therefore doubtless the stabler phase in comparison with the optically-active components, so that there is no chance to execute a fission by spontaneous crystallisation [1]. The solutions possess a beautiful orange or bloodred colour. For a series of wave-lengths the rotations were determined in the case of both antipodes; the values obtained agreed completely in both cases with exception of the algebraic sign. The concentrations of the solutions used in these experiments must be varied over wide limits, if measurements are to be made over a greater spectral range, because the absorption of the light in layers of 20 cm. is very intensive. In the visible part of the spectrum no distinct absorption-bands occur; but at both ends it is abruptly cut off· a 1,5 °/$_0$ solution allows the transmission of waves from 5190 to 6800 A. U.; a 0,75 °/$_0$ solution the transmission of the whole red, yellow, green, and blue part of the spectrum to 4870 A. U.; a 0,37 °/$_0$ solution in the same way to 4420 A. U.; etc. With a 1,48 °/$_0$ solution these limits were found at: 5020 and 6900 A. U.

For the polarimetric determinations we used solutions which contained respectively 1,503 grams (*A*), 0,511 grams (*B*), and 0.305 grams (*C*) of the *laevo*gyrate anhydrous salt in 100· grams of liquid; in the case of the *dextro*gyratory antipode we used a solution containing 0,804 °/$_0$ of the anhydrous salt. The results of these measurements are reviewed in the following table, and in fig. 2 they are plotted in a diagram. The data have been calculated with respect to the anhydrous salt.

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[1] Conf.: F. M. JAEGER, The Principle of Symmetry and Its Applications to All Natural Sciences, *Amsterdam*, (1917), p. 209, 210.

	ROTATION-DISPERSION OF LAEVO- AND DEXTROGYRATORY POTASSIUM-RHODIUM-MALONATE.							
Wave-length in A.U.	Observed (σ) and Molecular (M) rotations of the left salt:						Observed (σ) and Molecular (M) Rotations of the right salt:	
	A.		B.		C.		D.	
	α:	M:	σ	M:	$\alpha\cdot$	M	σ:	M.
4730	—	—	—	—	$-0,19°$	2436°	—	—
4870	—	—	—	—	0,19	2436	—	—
5020	—	—	—	—	0,19	2436	—	—
5105	—	—	$-0,49°$	$-2524°$	—	—	—	—
5180	—	—	0,49	2524	0,20	2564	—	—
5260	—	—	0,50	2575	—	—	—	—
5340	—	—	0,50	2575	0,20	2564	$+0,86°$	$+2614°$
5420	$-1,50°$	$-2621°$	0,51	2627	—	—	0,87	2645
5515	1,53	2673	0,52	2678	0,21	2692	0,88	2675
5610	1,59	2778	0,54	2781	—	—	0,90	2736
5700	1,61	2812	0,55	2833	0,22	2820	0,92	2797
5800	1,63	2847	0,56	2884	—	—	0,93	2827
5910	1,55	2708	0,53	2730	0,21	2692	0,89	2706
6020	1,47	2568	0,50	2575	—	—	0,85	2584
6140	1,44	2516	0,49	2524	0,20	2564	0,82	2493
6260	1,41	2463	0,48	2472	—	—	0,81	2462
6380	1,38	2410	0,47	2420	0,19	2436	0,74	2402
6520	1,35	2358	0,46	2369	—	—	0,78	2371
6660	—	—	0,45	2317	0,19	2436	—	—
6800	—	—	—	—	0,19	2436	—	—

From fig. 2 the very remarkable shape of the dispersion-curves may be seen, which at a wave-length of about 5800 A. U. show a maximum. For wave-lengths smaller than 5800 A. U. the rotation of the plane of polarisation increases with *increasing* wave-length, while for those greater than 5800 A. U. it diminishes with increasing

wave-lengths, as in ordinary cases. In the neighbourhood of 5800
A. U, the absorption-spectrum, however, does not manifest a single
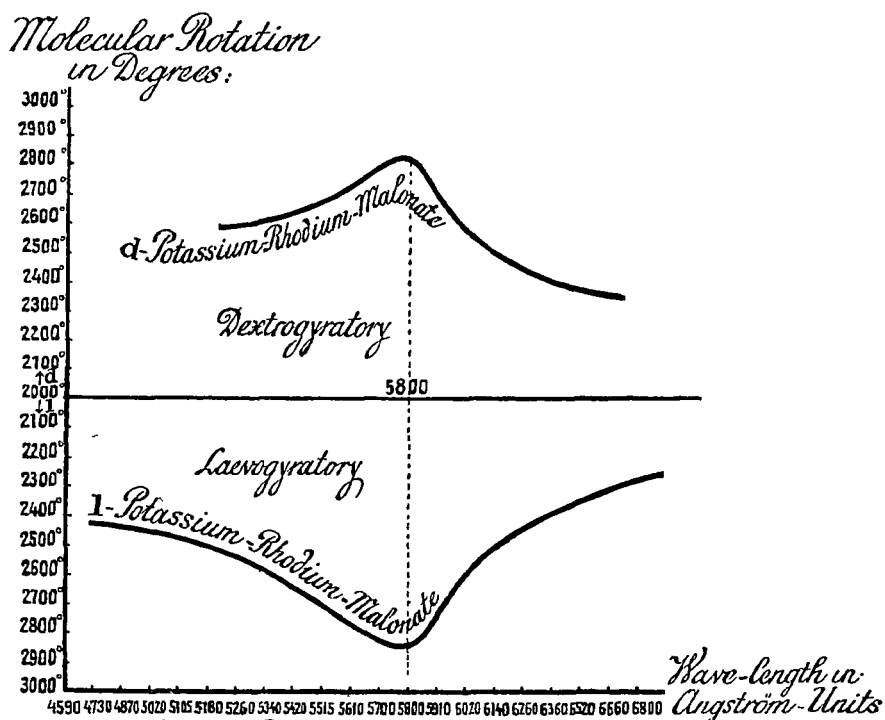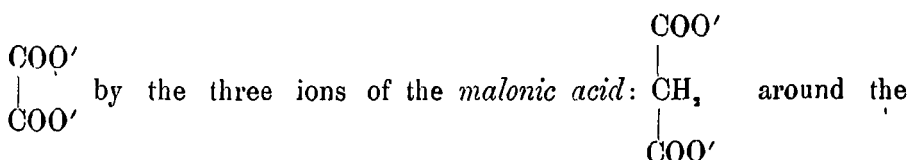line or band. However the occurrence of such an anomalous rotation-

Fig 2. *Molecular Rotation-Dispersion of dextro- and laevogyratory Potassium-Rhodium-Malonate.*

dispersion under these circumstances seems to be theoretically expli-
cable, if the assumption may be made that at least two kinds of
active ions are present [1]).

Besides this anomalous rotation-dispersion, the whole character of
which is in sharp contrast to that of the regular one, the *absolute*
activity of these salts appears in general to be appreciably *smaller*
than that of the analogously constituted *oxalates*, unregarded the
passing through the zero-point in the case of the *oxalate* at 5970
A. U., formerly mentioned. The substitution of the *oxalic acid*-ions:

$$\begin{matrix} COO' \\ | \\ COO' \end{matrix}$$ by the three ions of the *malonic acid*: $$\begin{matrix} COO' \\ | \\ CH_2 \\ | \\ COO' \end{matrix}$$ around the

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[1]) DRUDE, Lehrbuch der Optik, (1900), p. 382.

central *rhodium*-atom, is evidently followed by a very radical change of the character of the optical rotation of the molecule, which affects not only the magnitude, but also the algebraic sign of the molecular rotation for a number of corresponding wave-lengths. The special chemical nature of the substituents placed dissymmetrically round the central atom therefore appears to have as much influence on the magnitude of the rotation, as the chemical nature of the central metal-atom itself.

§ 4. After many attempts we were able to obtain the crystals of the optically-active salts in a measurable form. The laevogyratory component set free from the *cinchonine*-salt of the first fractions, appeared, as already mentioned, to be extremely soluble; the solutions manifested a strong tendency to supersaturation.

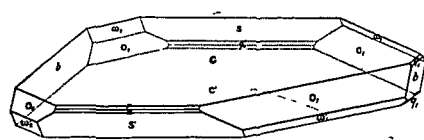By this circumstance the formation of well measurable crystals

Fig. 3. *Laevogyratory Potassium-Rhodium-Malonate.*

is severely ·hindered; and, as generally occurs in such · cases, the crystals finally obtained appeared to be badly formed. Because of the vicinal facets present, most crystal-faces yield multiple mirror-images, causing the angular values to oscillate often more than 30′ round their mean-values. Hence it was at first thought, that triclinic crystals were present here. But the repeated determinations, in connection with the optical investigation proved to us finally, that the salt crystallises monoclinically, and more especially in forms differing from their mirror-images.

The analogy of the parameters of the optically-active salt and those of the racemic compound is most remarkable, as becomes clear, if the directions of the *a*- and *c*-axes in our former determinations are interchanged [1]).

Monoclinic-sphenoidical

$$a : b : c = 1,0637 : 1 : 1,1667.$$

$$\beta = 85°27^{1}/_{4}'.$$

Forms observed: $c = \{001\}$, predominant, and mostly very lustrous; $b' = \{0\overline{1}0\}$, broad and lustrous; $b = \{010\}$, very narrow, often absent and always yielding good reflexes; $o_1 = \{111\}$, broad and lustrous; $\omega_1 = \{\overline{1}11\}$, narrower than o_1, yielding multiple reflexes; $o_2 = \{\overline{1}11\}$,

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[1]) F. M. JAEGER, Proceed. R Acad. Amsterdam, **20**. 277. (1917). There the ratio $a':b:c'$ was equal to: 1,0783: 1 : 1,2309; with $\beta = 86° 36'$.

and $\omega_2 = \{\overline{1}\,\overline{1}\,1\}$, about equally broad, giving sharp reflexes; $s = \{\overline{1}01\}$, broad and well reflecting, but as all faces of the orthodiagonal-zone, often showing oscillating angles; $r = \{101\}$; extremely narrow and dull; $a = \{100\}$, hardly observable, in most cases totally absent; $q = \{021\}$, very narrow and dull. The external habit is that of hemimorphic thin plates parallel to $\{001\}$, with a slight elongation in the direction of the b-axis.

No distinct cleavage could be found.

Angular Values:	Observed:	Calculated:
$b' : \omega_2 = (0\overline{1}0) : (\overline{1}\,\overline{1}\,1) =$	*50° 46'	—
$c : \omega_2 = (001) : (\overline{1}\,\overline{1}\,1) =$	*60 14	—
$c : o_2 = (001) : (1\,\overline{1}\,1) =$	*55 45	—
$c : a = (001) : (1\,0\,0) =$	85 41	85° 27^1/$_4$'
$c : s = (001) : (\overline{1}\,0\,1) =$	50 4	50 8
$o_1 : \omega'_1 = (111) : (1\,\overline{1}\,1) =$	64 5	64 1
$s : \omega_2 = (\overline{1}01) : (\overline{1}\,\overline{1}\,1) =$	39 23	39 14
$q : c = (012) : (0\,0\,1) =$	ca. 31 0	30 11
$b' : o'_2 = (0\overline{1}0) : (\overline{1}\,\overline{1}\,\overline{1}) =$	52 49	52 58

On $\{001\}$ the directions of extinction are orientated parallel to and normal to the orthodiagonal. The crystals are not appreciably dichroitic; their birefringence is feeble. The optical axial plane is $\{010\}$, with a feeble, inclined dispersion; one axis emerges on $\{001\}$ at the border of the field.

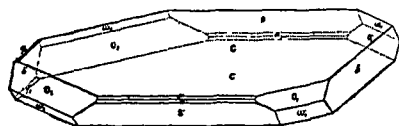The crystal-form of the corresponding dextrogyratory antipode is reproduced in fig. 4.

Fig. 4. *Dextrogyratory Potassium-Rhodium-Malonate.*

The specific gravity of the crystals was at 18° C. found to be: $d_4^{18°} = 2,317$; the molecular volume is therefore: 238,76, and the topical parameters become: $\chi : \psi : \omega = 6,1471 : 5,7790 : 6,7423$. Analysis proved that the salt contains $1\frac{1}{2}$ H_2O; on heating at 120° C. it is decomposed, assuming a brown colour.

If the specific gravity of the racemic compound be also taken into account, ($d_{18°}^{4°} = 2,251$; $V = 257,80$), it appears, in comparing it with the corresponding *potassium-rhodium-oxalate* [1]), that the sub-

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[1]) The topical parameters of the *racemic malonate*, after interchange of the a- and c-axis, becomes: $\chi : \psi : \omega = 6,2484 : 5.7947 : 7,1329$.

stitution of the *malonic acid* for the oxalic acid, causes a diminution of the topical parameters in two, but an enlargement in the third direction as well in the case of the racemic as in that of the optically-active compounds.

At all events this investigation has brought full evidence of the fact, that the salts of the complex *rhodium-trimalonic acid* may also be split into optically-active components, and that the phenomena observed in their study are in agreement with PASTEUR's law in its fullest scope.

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