Chemistry. — "*Investigations on* Pasteur's *Principle concerning the Relation between Molecular and Crystallonomical Dissymmetry: VII. On optically active Salts of the Tri-ethylenediamine-Chromi-series*." By Prof. F. M. Jaeger and William Thomas.

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

§ 1. Some time ago it was already found [1]) by one of us, that *racemic tri-ethylenediamine-chromichloride*: $\{Cr(En e)_3\}Cl_3 + 3H_2O$, was completely isomorphous with the corresponding *cobalti-* and *rhodium-*compounds. We prepared this salt according to a method indicated by Pfeiffer [2]), from the *tripyridyl-chromi-chloride*: $\{Cr(Pyr.)_3\}Cl_3$ by heating this product with ethylenediamine, and subsequent purification. Then it was separated into its optical antipodes by means of *sodium-a-camphor-nitronate* [3]), and these were obtained in this way as the pure *iodides*.

In this fission 6 grams of the racemic salt were dissolved in 20 ccm water, and a solution of 6 grams of pure *sodium-a-camphor-nitronate* in 15 ccm water subsequently added. A pale yellowish precipitate of *d-triethylenediamine-chromi-d-camphornitronate* is formed; it is sucked off and to the mother liquid 2 more grams of *sodium-a-camphornitronate* are then added, and the solution allowed to stand for a few hours, when some more of the precipitate is separated.

After filtration the mother liquid was used for preparing the corresponding laevogyratory component. The precipitate, thoroughly washed with alcohol and ether, was ground in a mortar with an excess of finely pulverised *sodium-iodide*, some water added, and the dark yellow liquid sucked off from the precipitate, which was well washed with alcohol and ether, dissolved in a small quantity of water, and again precipitated by an excess of *sodium-iodide*.

The mother liquid formerly mentioned, containing the *camphor-nitronate* of the *laevogyrate* salt, was precipitated by addition of 5 grams *sodium-iodide*. The precipitate formed appeared, after being thoroughly washed, to be the *racemic iodide*. The remaining

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[1]) F. M. Jaeger, Proceed. R. Acad., Amsterdam. **20**. 247. (1917).

[2]) P. Pfeiffer, Zeits. f. anorg. Chemie, **24**. 282, 286. (1900).

[3]) A. Werner, Ber. d deutsch Chem. Ges. **45**. 865. (1912).

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mother liquid, however, was now treated in an analogous way with 8 grams of sodium-iodide; the precipitate appeared to be this time the *laevogyrate triethylenediamine-chromi-iodide*. It is difficult to obtain these iodides in well measurable crystals, and they are moreover ordinarily very small.

§ 2. The rotation-dispersion of these salts was determined in the usual way, already frequently indicated. As the orange coloured liquids already manifested a very appreciable absorption of the transmitted light in layers of 20 c.m. thickness, the measurements for the limiting wave-lengths had to be made with very dilute solutions. These measurements agreed very well with those made in the case of more concentrated solutions, so that for all solutions we have given the mean values of the molecular rotations obtained. In the case of the dextrogyratory component solutions were used, containing 1,0133 grams (A), 0,5070 grams (B), 0,2535 grams (C), and 0,0325 grams (D) of the anhydrous salt respectively in 100 grams
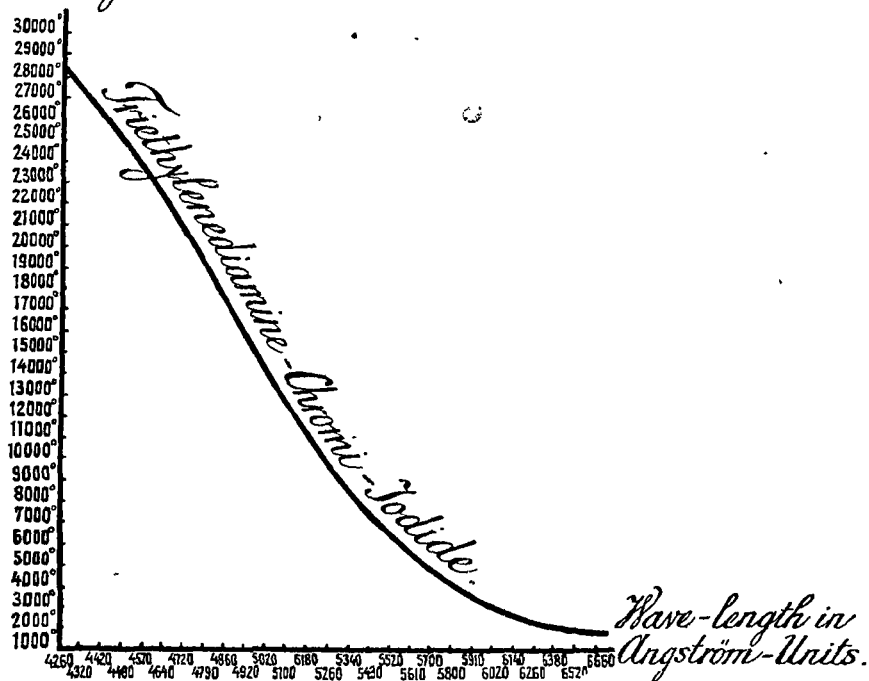
Fig. 1. Molecular Rotation-Dispersion of the Optically active Triethylenediamine-Chromi-Iodides.

Wave-length in A. U.:	Observed Rotation:		Molecular Rotation: (positive and negative)
	ROTATION-DISPERSION OF THE OPTICALLY-ACTIVE TRI-ETHYLENEDIAMINE-CHROMI-IODIDES.		
- 4260	0.°30	(D)	28263°
4320	0 29	id.	27321
4420	0.27; 0.35	(D, K)	25385
4480	0.26; 0.34	id.	24552
4570	0.25; 0.33	id.	23619
4640	0.23; 0.31	id.	22053
4720	0.22; 0.29	id.	20858
4790	0.20; 0.28; 0.27	(D, I, K)	18652
4860	0.18; 0.26; 0.24	id.	17610
4920	0.16; 0.23; 0.21	id.	15128
5020	0.14; 0.40; 0.21	(D, H, I)	13267
5100	0.97; 0.36; 0.18	(C, H, I)	11714
5180	0.88; 0.32; 0.16	id.	10579
5260	1.60; 0.79; 1.07	(B, C, G)	9647
5340	1.43; 0.71; 0.95	id.	8578
5430	1.27; 0.64; 0.84	id	7634
5520	1.12; 0.57; 1.46; 0 72	(B, C, F, G)	6692
5610	0.96; 0.48; 1.22; 0.62	id.	5741
5700	1.63; 0.81; 0.41; 2.18	(A, B, C, E; F, G)	4891
5800	1.33; 0.67; 0.33; 1.85	id.	4093
5910	1.15; 0.56; 0 28; 1.55	id.	3422
6020	0.96; 0.47; 0.24; 1.30 id.	For these last wave-lengths only the rota-tions of the solutions A, B, C, and E are reviewed.	2912
6140	0.86; 0.43; 0.22; 1.16 id.		2621
6260	0.77; 0.38; 0.19; 1.04 id.		2328
6380	0.70; 0.35; 0.18; 0.94 id.		2133
6520	0.65; 0.32; 0.16; 0.88 id.		1951
6660	0.61; 0.30; 0.15; 0.82 id.		1820

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of the liquid; in the case of the laevogyrate antipode the six different solutions employed contained 1,3512 grams (E), *half* or a *quarter* of this (F, G) in 100 grams of the liquid, and 0,0927 grams (H), 0,0464 grams (I), and 0,0232 grams (K) respectively of the anhydrous salt in 100 grams of the liquid.

The dispersion-curve for the molecular rotation, shewn by measurements is plotted in the diagram (fig. 1). It has much analogy with that of the corresponding *cobalti*-salts, but only a slight analogy with that of the *triethylenediamine-rhodium*-compounds.

Probably the magnitude of the rotation for corresponding wave-lengths in the case of these analogously built complex ions greatly depends on the magnitude of the *atomic volume* of the central metallic atom, in such a way that the rotation appears *higher*, if the atomic volume of the metal is *smaller*. As for instance:

COMPLEX SALT:	MOLECULAR ROTATION OBSERVED:	ATOMIC VOLUME OF THE METAL
{Co (Eïne)₃} I₃ + H₂O.	$M_{5800} = 7230°$; $M_{5100} = 21580°$; $M_{6600} = 2114$?	6.76
{Cr (Eïne)₃} I₃ + H₂O.	$M_{5800} = 4093°$; $M_{5100} = 11714°$; $M_{6600} = 1880°$	7.72
{Rho (Eïne)₃} I₃ + H₂O.	$M_{5800} = 3125°$; $M_{5100} = 3965$; $M_{6600} = 2243$?	8.50

The values for $\lambda = 6600$ A. U., are mentioned at the same time for the purpose of demonstrating that this antiparallelism of rotations and atomic volume is surely *not* true for *all* wave-lengths: for rays of *great* wave-length, as e. g. in the visible red part of the spectrum, — the rotation of the *Rho*-salt surpasses even that of both the other salts; only in the domain of appreciable dispersion, is the said regularity met with.

As regards the absorption, we were able to state the following. In a layer of the solution of 20 c.m., a liquid containing.

1,1212% of the salt, allows the passage of all red and yellow rays up to those of 5380 A.U.
0,5606% „ „ „ „ „ „ „ „ „ „ „ „ „ „ „ 5220 A.U.
0,2803% „ „ „ „ „ „ „ „ „ „ „ „ „ „ „ 5030 A.U.
0,1402% „ „ „ „ „ „ „ „ „ „ „ „ „ „ „ 4850 A.U.
0,0701% „ „ „ „ „ „ „ „ „ „ „ „ „ „ „ 3940 A.U.

§ 3. Numerous attempts were made to win these *chromi*-salts in well measurable crystals, and to investigate the validity of PASTEUR's law also in this case. But a heavy impediment in reaching this aim was created not only by the facility with which those salts decompose in solution, especially under the influence of the light, — but also

by the great solubility of these salts, inducing us always to work with only small volumes of concentrated solutions, from which good crystals are ordinarily deposited with difficulty. For the same reason the transformation of the iodide into the chloride or bromide could not be of any use, so that these for our purpose so very important salts, could not be made use of in this case.

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RACEMIC TRIETHYLENEDIAMINE-CHROMI-IODIDE.

$\{Cr\,(Eine)_s\}\,I_s + 1H_2O.$

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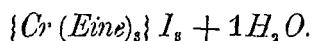
On slow crystallisation this compound presents itself in the form of very small, orange, apparently octahedral crystals. Crystallisation must occur in the dark, because this salt, in the same way as all the *triaethylenediamine-chromi-salts*, becomes violet under the influence of the light. Also increase of temperature must be avoided, because the solutions change from an orange colour to a dark reddish violet by the transformation into salts of the violet *aquo*-type. The crystals measured were not larger than a pinhead, and often they were disfigured and distorted in rather a strange way. Some of them showed under the microscope the appearance of fig. 2a, without
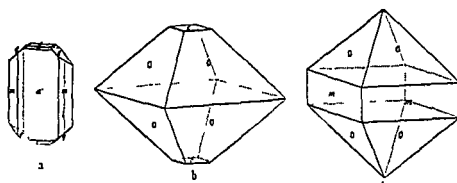

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Fig. 2. *Racemic Triethylenediamine-Chromi-Iodide.* $(+ H_2O)$.

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it being possible however to determine the MILLERian indices of their facets with complete certainty; the crystals pictured in fig. 2b and 2c manifested however some measurable forms.

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- *Rhombic-bipyramidal.*

$a:b:c = 0{,}8632 : 1 : 0{,}8652.$

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The crystals are pseudo-tetragonal, and perfectly isomorphous with the corresponding crystals of the *cobalti*-[1]), and of the *rhodium*-[2]) compound, just as we were able to prove this before in the case of the trigonal *chloride* of this series [3]). The colour of the crystals was orange or red; by partial loss of water of crystallisation, they sometimes get locally yellow and opaque.

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[1]) F. M. JAEGER, Proceed. R. Acad. Amsterdam, **18**. 62 (1915).

[2]) F. M. JAEGER, Proceed. R. Acad. Amsterdam, **20**. 250. (1917)

[3]) F. M. JAEGER, Proceed. R. Acad. Amsterdam, ibid. 247. (1917).

The forms observed are: $o = \{111\}$, great and very lustrous; $c = \{001\}$, small, but well developed and yielding good reflections; $m = \{110\}$, broad, but commonly with curved and rudimentary facets, and thus practically not well measurable. Probably also a form $q = \{021\}$ occurs, and in the case of the crystals of fig. $2a$ doubtless· $a = \{100\}$, as a broad pinacoidal face, and $r = \{h\,o\,k\}$.

Angular values:	Observed:	Calculated:
$c : o = (001) : (111) =$	$*52° \ 56'$	—
$p : o = (111) : (1\bar{1}1) =$	$62 \ 49$	—
$o \cdot o = (111) : (11\bar{1}) =$	$74 \ 10$	$74° \ 8'$
$o : o = (111) : (\bar{1}11) =$	$74 \ 27$	$74 \ 19$

No distinct cleavability was found.

There cannot be the least doubt about the complete isomorphism with the corresponding *Co-* and *Rho-*salt:

$$Cr\text{-salt} \ldots \ldots a : b : c = 0,8632 : 1 : 0,8652.$$
$$Co\text{-salt} \ldots \ldots a \cdot b : c = 0,8700 : 1 : 0,8699.$$
$$Rho\text{-salt} \ldots \ldots a : b : c = 0,8541 : 1 : 0,8632.$$

Up till now we have had no opportunity to prove this isomorphism also in the case of the optical antipodes, because no suitable crystals could be obtained. There can be however no doubt, that the said relation also exists in this case.

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