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**Chemistry.** — “Investigations into PASTEUR’S Principle of the Connection between Molecular and Crystallonomical Dissymmetry: **III.** Racemic and Optically Active Complex Salts of Trivalent Rhodium. By Prof. Dr. F. M. JAEGER.

(Communicated in the meeting of June 30, 1917.)

§ 1. In immediate continuation of previous investigations concerning the complex *tri-ethylenediamine*-salts of trivalent *cobaltum*<sup>1)</sup>, the results of the study of the corresponding complex salts of trivalent *rhodium* are communicated in the present paper, namely in so far as the data already obtained possibly allow a more general discussion of some problems connected with this subject.

For the preparation of the salts investigated, we started from pure *rhodium-trichloride*. Originally WERNER’S method<sup>2)</sup> was followed, who transformed the *chloride* into *sodium-rhodium-chloride*:  $\text{Na}_3\{\text{Rho Cl}_6\} + 12 \text{H}_2\text{O}$ , which afterwards was dissolved in gently heated *ethylenediamine-hydrate*. It appeared, however, that the troublesome purification of the complex salt from the adhering *sodiumchloride* may be prevented, when the *rhodium-trichloride* itself is dissolved immediately into the base mentioned, on gently heating it with the last. If some few precautions be taken, the required substance is obtained from an aqueous solution immediately in very beautiful, colourless crystals. It must, moreover, be remarked in this connection, that a miscibility between the complex *rhodium-salt* and *sodium-chloride* in the solid state, as supposed by the author mentioned because of an eventually existing isomorphism of two crystal-species of cubic symmetry, does in reality *not* occur. No such isomorphism is present here, as the complex *rhodium-salt* has *ditrigonal*, the *sodium-chloride* on the contrary *cubic* symmetry. Probably only occlusion or mechanical removal of the one salt by the other may be the cause of the phenomenon observed. Moreover, it must appear remarkable, that almost all data concerning the amount of water of crystallisation present in these *rhodium-salts*, differ exactly by the number of *half* a molecule  $\text{H}_2\text{O}$  in comparison with those of the corresponding *cobalti-salts*. As the last mentioned salts are, however,

<sup>1)</sup> F. M. JAEGER, *Proceed. Kon. Akad. Amsterdam*, **17**. 1217; **18**. 49. (1915); *Zeits. f. Kryst. u. Miner.* **55**. 209. (1915).

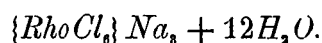
<sup>2)</sup> A. WERNER *Ber. d. d. Chem. Ges.* **45**. 1228. (1912).

in by far the most cases, *directly isomorphous* with the *rhodium*-salts of corresponding constitution, suspicion arises that the content of crystallisation-water is really the same in the two series of complex salts. The divergence mentioned would then be explained by a systematical error in the rather difficult determinations of the element *rhodium* in these cases.

§ 2. In the following pages the result of the direct measurements of the *racemic* salts and of the *optically active* components are in the first place dealt with, and the data concerning the rotation-dispersion of these perfectly colourless salts are subsequently communicated. Some considerations of a more general character, regarding the stereometrical configuration of these complex substances will then be inserted.

The results of the study of some other compounds of this series will be published later-on.

#### SODIUM-RHODIUM-CHLORIDE.



This salt may be prepared by dissolving the calculated quantity of *rhodium-trichloride* in a concentrated solution of *sodium-chloride*, evaporating the solution on the water-bath, and by crystallisation at room-temperature. The solution of the black-red, often voluminous

and apparently octahedral crystals, has a beautiful crimson colour. The crystals are hygroscopical, and they soon become dull, when softly heated.

Monoclinic-prismatic.

$$a : b : c = 1,2034 : 1 : 1,4576 ;$$

$$\beta = 57^\circ 9\frac{1}{2}'$$

*Forms observed:*  $c = \{001\}$ , small but lustrous; ordinarily the facet  $(00\bar{1})$  appears much broader than  $(001)$ ;  $r_1 = \{101\}$ ,  $r_2 = \{\bar{1}01\}$ , and  $q = \{011\}$ , commonly equally well developed,

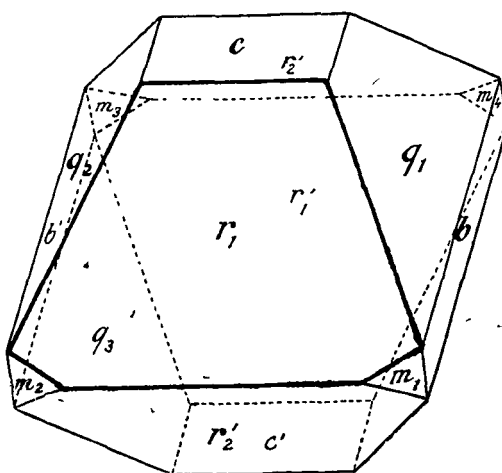


Fig. .1

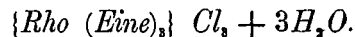
Sodium-Rhodium-Chloride.

and giving good images;  $b = \{010\}$ , narrow, mostly absent;  $s = \{021\}$ , very narrow, often absent, but sharply reflecting;  $m = \{430\}$ , small, dull, and often absent. The external shape is apparently octahedral, and isometrically developed.

<i>Angles.</i>	<i>Observed</i>	<i>Calculated:</i>
$c : r = (001) : (101) = ^\circ$	71°32'	—
$r_1 : r_2' = (101) : (10\bar{1}) = ^\circ$	63 8	—
$c : q = (001) : (011) = ^\circ$	50 46	—
$c : r = (001) : (101) =$	45 30	45°20'
$q : q = (011) : (01\bar{1}) =$	78 28	78 28
$b : q = (010) : (011) =$	39 20	39 14
$r : q = (101) : (011) =$	63 47	63 41
$r : q = (\bar{1}01) : (011) =$	77 0	77 4
$c : s = (001) : (021) =$	67 56	67 47½
$b : m = (010) : (430) =$	52 40	52 49
$m : m = (430) : (4\bar{3}0) =$	74 40	74 22

The crystals are cleavable parallel to {001}.

### § 3. RACEMIC TRI-ETHYLENEDIAMINE-RHODIUM-CHLORIDE.



The salt was prepared from the corresponding *iodide* in solution, by treating it with freshly precipitated *silver-chloride*. The substance crystallises in big, rectangular-shaped, prismatic individuals, or in smaller, strongly refracting crystals, which often possess uneven faces yielding multiple reflexes.

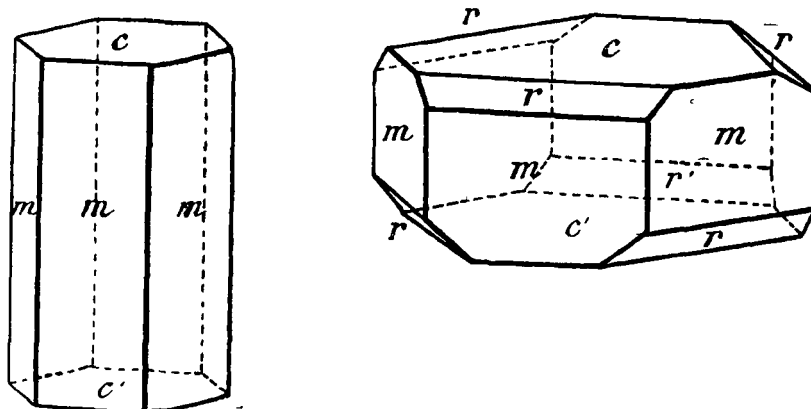


Fig. 2.

Racemic Tri-ethylenediamine-Rhodium-Chloride.

*Ditrigonal-scalenohedral.*

$$a : c = 1 : 0.6730.$$

*Forms Observed:*  $c = \{0001\}$ , predominant, often rough, but lustrous;  $m = \{10\bar{1}0\}$ , well developed, always present, and lustrous;  $r = \{10\bar{1}1\}$ , narrow, often absent;  $x = \{1\bar{1}01\}$ , smaller than  $r$ , and only rarely present. The crystals are plates parallel to {0001}, or prisms parallel to the  $c$ -axis.

The substance is perfectly isomorphous with the corresponding

*Co*-salt<sup>1)</sup>); WERNER's supposition of their being cubic and isomorphous with *NaCl*, is erroneous, as has been already said.

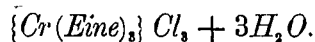
Angles:	Observed:	Calculated:
$c:r = (0001):(10\bar{1}1) =^*$	$37^\circ 51'$	—
$m:r = (10\bar{1}0):(1011) =$	$52 \quad 9$	$52^\circ 9'$
$m:m = (10\bar{1}0):(01\bar{1}0) =$	$60 \quad 0$	$60 \quad 0$
$c:x = (0001):(1\bar{1}01) =$	$38 \quad 1$	$37 \quad 51$

No distinct cleavability was found.

The crystals are uniaxial, their birefringence is negative. The interference-image is sometimes slightly disturbed, as was observed also in the case of the *Co*-salt.

The corresponding *bromide* was completely isomorphous with the *chloride* here described.

#### § 4. RACEMIC TRI-ETHYLENEDIAMINE-CHROMI-CHLORIDE.



Beautiful, orange, very transparent and lustrous prismatic crystals, which commonly only exhibit the forms *c* and *m*. Occasionally also hexagonal plates occur parallel to {0001}; once a form  $r = \{10\bar{1}1\}$  was observed as a very narrow truncation of the edge  $c:m$ .

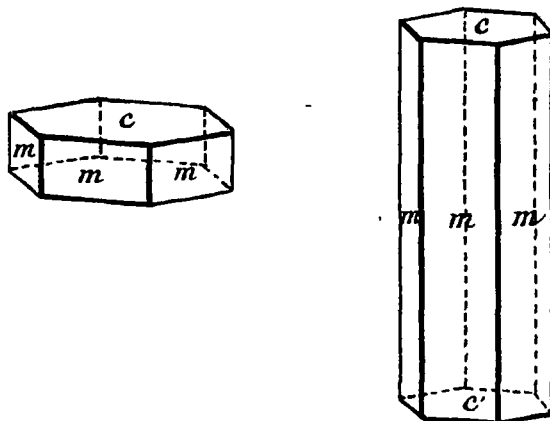


Fig. 3  
Racemic Tri-ethylenediamine-chromi-chloride.

*Ditrigonal-scalenohedral.*

$$a:c = 1:0,6930.$$

*Forms observed:*  $c = \{0001\}$ , and  $m = \{10\bar{1}0\}$ , both very lustrous, while sometimes *c*, sometimes however *m* is developed predominantly;  $r = \{10\bar{1}1\}$ , mostly absent, and in all cases very narrow.

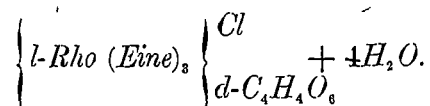
<sup>1)</sup> F. M. JAEGER, *Proceed. Kon. Acad. Amsterdam*, 18. 50. (1915).

Angles:	Observed:	Calculated:
$c:r = (0001) : (10\bar{1}1) = *$	$38^\circ 40'$	—
$r:m = (1011) : (10\bar{1}0) =$	$51 \quad 20$	$51^\circ 20'$
$m:m = (10\bar{1}0) : (0110) =$	$60 \quad 0$	$60 \quad 0$

No distinct cleavability was observed.

The crystals show a feeble dichroism: on  $m$  they are orange-yellow for vibrations parallel to the  $c$ -axis, and lemon-yellow for such as are perpendicular to that direction. Optically uniaxial, occasionally with disturbed interference-image. The character of birefringence is negative as it was in the cases of the *Co*-, and *Rho*-salts.

§ 5. LAEOGYRATE TRI-ETHYLENEDIAMINE-RHODIUM-  
-CHLORO-D-TARTRATE.



Beautiful, rather big colourless and parallelogram-shaped plates or short prisms. They are well developed and possess constant angular values.

*Monoclinic*, and having apparently *prismatic* symmetry. Of the facets of  $o$  and  $\omega$  commonly only three, e.g.  $\omega_2$ ,  $o_2$  and  $o_4$ , are present.

$$a:b:c = 0,9158:1:0,6965;$$

$$\beta = 72^\circ 35\frac{2}{3}'.$$

*Forms observed*:  $m = \{110\}$ , well developed, commonly predominant with two parallel faces and having high lustre;  $c = \{001\}$ , large and also perfectly reflecting;  $\omega = \{\bar{1}11\}$ , larger than  $o = \{111\}$ , both rather dull and giving weak reflections. The crystals are plates parallel to  $\{110\}$ , with a slight elongation in the direction of the  $c$ -axis.

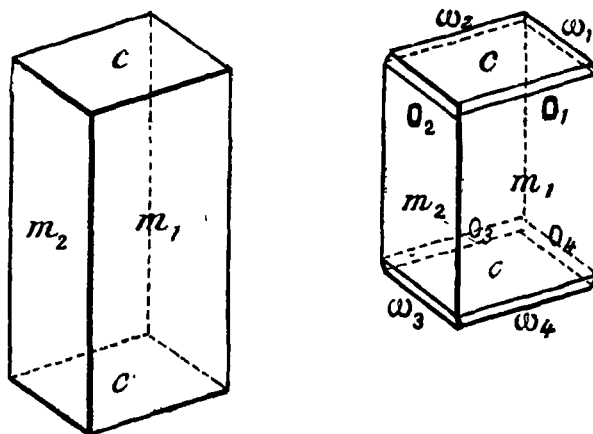


Fig. 4.

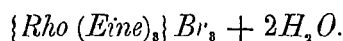
l-Tri-ethylenediamine-rhodium-chloro-d-tartrates.

Angles:	Observed:	Calculated:
$c:m = (001):(110) = ^\circ$	76° 59'	—
$m:m = (110):(\bar{1}\bar{1}0) = ^\circ$	82 18	—
$c:o = (001):(\bar{1}\bar{1}1) = ^\circ$	51 53	—
$m:o = (\bar{1}\bar{1}1):(\bar{1}\bar{1}0) =$	51 8	51° 8'
$c:o = (001):(111) =$	38 40	38 43
$m:o = (110):(111) =$	38 19	38 16
$m:\bar{o} = (\bar{1}\bar{1}1):(110) =$	86° circa	85 40

Cleavage parallel to  $c$  and  $m$ .

On  $\{110\}$  the extinction-angle is small, only  $5^\circ$ — $10^\circ$  with respect to the edge  $m:m$ . The plane of the optical axes is  $\{010\}$ .

§ 6. LAEVOGYRATE TRI-ETHYLENEDIAMINE-RHODIUM-BROMIDE.



The substance was prepared from pure laevogyrate *iodide* by heating its solution with freshly precipitated *silver-bromide*. After filtration the solution was concentrated on the water-bath, and crystallised at room-temperature. Very big, hexagonal thick plates are deposited from the colourless solution, which are strongly refracting and give extremely sharp reflexes.

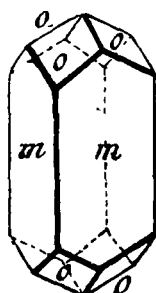


Fig. 5.

Laeogyrate Triethylene-diamine-  
Rhodium-Bromide.

*Ditetragonal*, apparently *bipyramidal*, and completely isomorphous with the corresponding *cobalti-salt*.

$$a:c = 1:0,8330.$$

*Forms observed*  $m = \{110\}$ , ordinarily with two predominant parallel faces, very lustrous, but often uneven;  $o = \{101\}$ , splendidly reflecting and with well-developed faces. The shape of

the crystals is that of thick plates parallel to faces of the prism; elongation parallel to the  $c$ -axis. No *indication of hemihedrism* was observed in any case, just as was stated in the case of the corresponding *cobalti-salts*.

Angles:	Observed:	Calculated:
$o:o = (101):(011) = ^\circ$	53° 49'	—
$o:m = (101):(110) =$	63 5½	63° 5½'
$m:m = (110):(\bar{1}\bar{1}0) =$	90 0	90 0

No distinct cleavability was observed.

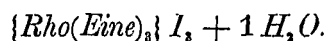
The crystals are optically uniaxial; a plate perpendicular to the

*c*-axis shows in convergent polarised light the axial image characteristic of uniaxial crystals *without circular polarisation*. The character of the birefringence is negative.

## § 7.

<b>Rotation-Dispersion of Laevogyrate Tri-ethylenediamine-Rhodium-Bromide.</b> The solution contained 7,310 grams of the anhydrous salt in 100 grams of the solution. The length of the tube applied was 20 c.m.		
Wave-length in ÅNGSTRÖM-Units	Specific Rotation $[\alpha]$ in Degrees	Molecular rotation $[M]$ in Degrees.
6780	— 46,66	— 2440°
6640	— 48,0	— 2510
6520	— 49,66	— 2597
6380	— 53,08	— 2776
6260	— 56,57	— 2960
6140	— 59,0	— 3086
6030	— 62,66	— 3277
5890	— 66,1	— 3457
7500	— 71,07	— 3717
5510	— 76,40	— 3996
5340	— 81,33	— 4253
5180	— 85,30	— 4461
5100	— 87,62	— 4583
4860	— 91,93	— 4808
4710	— 94,60	— 4947
4310	— 97,20	— 5083
4150	— 97,34	— 5091

## § 8. RACEMIC TRI-ETHYLENEDIAMINE-RHODIUM-IODIDE.



Very small, colourless, strongly refracting and well-developed crystals, which are completely isomorphous with the corresponding *cobalti-salt*<sup>1)</sup>. In the last case, however, the symbol {111} was

<sup>1)</sup> F. M. JAEGER, Proceed. 18. 62. (1915).



attributed to the form  $w = \{112\}$ , so that the value of  $b:c$  in the former case is analogous to  $b:2c'$  in the present.

*Rhombic-bipyramidal.*

$$a : b : c = 0,8541 : 1 : 0,8632.$$

*Forms observed:*  $o = \{111\}$ , predominant and very lustrous;  $c = \{001\}$ , also well-developed and giving splendid reflexes;  $w = \{221\}$ , very narrow, but exactly measurable;  $q = \{041\}$ , small, very lustrous, and often absent.

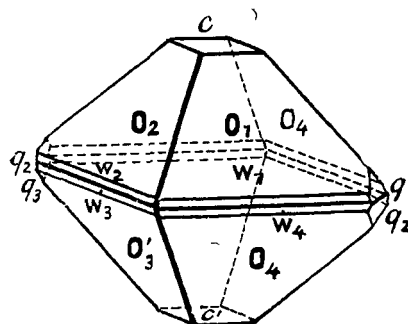


Fig. 6.

Racemic

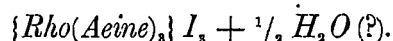
Tri-ethylenediamine Rhodium Iodide

Angles:	Observed.	Calculated:
$c : o = (001) : (111) =^*$	$53^\circ 3'$	—
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =^*$	$74 51$	—
$o : w = (111) : (221) =$	$16 11$	$16^\circ 20'$
$w : w = (221) : (2\bar{2}\bar{1}) =$	$41 33$	$41 14$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$73 55$	$73 54$
$o : o' = (111) : (\bar{1}\bar{1}\bar{1}) =$	$62 43$	$62 43$
$o : q = (111) : (041) =$	$47 59$	$48 16$
$q : w = (041) : (2\bar{2}\bar{1}) =$	$60 52$	$60 56$
$w : o = (2\bar{2}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	$70 52$	$70 48$

No distinct cleavage was found.

When considered as a rhombic, but pseudo-tetragonal crystal,  $c$  becomes  $\{100\}$ , and  $a : b : c = 1,0106 : 1 : 1,1708$ .

§ 9. LAEVOGYRATE TRI-ETHYLENEDIAMINE-RHODIUM-IODIDE.



Small, colourless and only feebly reflecting crystals, which are however well measurable and possess constant angular values. Occasionally very lustrous, nicely shaped and regularly developed little crystals were met with.

*Rhombic*; perhaps *bisphenoidical*, although the geometrical appearance is completely holohedral.

$$a : b : c = 0,8064 : 1 : 0,7380.$$

*Forms observed:*  $c = \{001\}$ , well-developed and lustrous;  $o = \{121\}$ , and  $\omega = \{1\bar{2}1\}$ , almost equally large, and only very rarely  $\omega$  somewhat broader than  $o$ . This different size of  $o$  and  $\omega$  is the only indication of the substance eventually being bisphenoidical. Further:

17\*

$r = \{101\}$ , smaller than  $s = \{201\}$  and  $a = \{100\}$ ;  $t = \{021\}$  and  $w = \{041\}$ , both equally large and greater than  $b = \{010\}$ ;  $q = \{011\}$ , commonly absent, but if present, rather large,  $m = \{110\}$ , absent in almost every case, always small and receding into the background

Undoubtedly the crystals are isomorphous with those of the optically active *cobalti*-salts, whose expected bisphenoidical symmetry did not reveal itself in any distinct way either. The rather appreciable divergence of the values  $a$   $b$  of the salts, as well as the differences in shape and combined forms in the two cases, may probably be connected with the eventually existing slight difference in the content of water of crystallisation, mentioned previously.

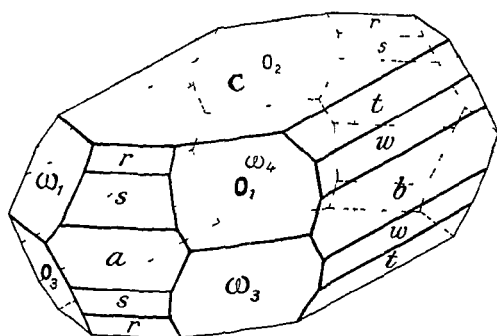


Fig. 7 (1).

Laevogyrate

Tri ethylenediamine Rhodium-Iodide.

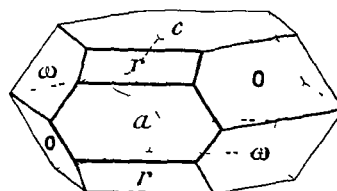


Fig. 7 (2).

Laevogyrate

Tri-ethylenediamine Rhodium Iodide.

<i>Angles:</i>	<i>Observed</i>	<i>Calculated:</i>
$c:t = (001):(021) = ^* 55^\circ 53'$		—
$c:o = (001):(121) = ^* 60^\circ 4'$		—
$t:w = (021):(041) = 15\ 26$		$15^\circ 24\frac{1}{4}'$
$w:b = (041):(010) = 18\ 46$		$18\ 42\frac{3}{4}$
$c:r = (001):(101) = 42\ 21$		42 28
$r:s = (101):(201) = 18\ 54$		18 53
$s:a = (201):(100) = 28\ 45$		28 39
$o:o = (121):(\overline{121}) = 59\ 52$		59 52
$o:o = (\overline{121}):(\overline{121}) = 85\ 10$		85 8
$a:o = (100):(121) = 62\ 45$		62 50
$b:o = (010):(\overline{121}) = 42\ 40$		42 34
$t:o = (021):(\overline{121}) = \text{—}$		$27\ 10\frac{1}{3}$
$w:o = (041):(\overline{121}) = 57\ 40$		$57\ 29\frac{1}{3}$
$b:q = (010):(011) = 53\ 26$		53 34
$o:w = (121):(\overline{121}) = 54\ 26$		54 20

No distinct cleavability could be observed.

The external aspect of the crystals is almost isometrical, with a slight flattening parallel to {001}, and a distinct elongation parallel to the direction of the direction of the  $\alpha$ -axis.

The optical axes are situated in  $\{001\}$ ; the  $a$ -axis is first bisectrix.

## § 10.

**Rotation-dispersion of laevogyrotory Tri-ethylenediamine-rhodium-iodide.**

The solution investigated contained 4,535 grams anhydrous salt in 100 grams of solution; the length of the tube applied was 20 c.m.

<i>Wave-length in ANGSTRÖM-Units:</i>	<i>Specific rotation [α] in Degrees.</i>	<i>Molecular rotation [M] in Degrees:</i>
6840	— 30,91	— 2051°
6660	— 32,89	— 2183
6520	— 34,98	— 2322
6380	— 37,18	— 2468
6260	— 38,50	— 2555
6140	— 41,14	— 2730
6030	— 44,11	— 2928
5890	— 45,54	— 3023
5800	— 47,08	— 3125
5700	— 49,06	— 3256
5605	— 50,49	— 3351
5510	— 52,36	— 3475
5420	— 54,12	— 3592
5340	— 55,22	— 3665
5260	— 57,20	— 3796
5180	— 58,30	— 3869
5100	— 59,73	— 3964
5020	— 61,05	— 4052
4945	— 61,93	— 4110
4860	— 63,36	— 4205
4780	— 64,46	— 4278
4710	— 65,34	— 4337
4650	— 66,66	— 4424
4560	— 67,32	— 4468
4480	— 67,87	— 4505
4420	— 68,42	— 4541
4310	— 68,53	— 4548
4260	— 68,64	— 4556
4150	— 68,82	— 4567
4060	— 69,10	— 4585
4010	— 69,19	— 4592
3940	— 69,24	— 4596
3880	— (60,5)	— (4016)
3820	— (55,2)	— (3664)
3780	— (51,2)	— (3398)
3740	— (48,7)	— (3232)
3700	— (48,5)	— (3219)

practically  
constant

uncertain  
measurements

§ 11. RACEMIC TRI-ETHYLENEDIAMINE-RHODIUM-NITRATE.  
 $\{Rho(Eine)_3\}(NO_3)_3$ .

This compound is always obtained, when a solution of the racemic chloride is mixed with a solution of  $AgNO_3$ . It crystallises from an aqueous solution in splendid, colourless, and distinctly *hemimorphic* crystals, showing a strongly variable aspect, and often distorted in a most particular way. Some of the forms most often met with are reproduced in fig. 8 *a*, *b*, and *c*. For the purpose of immediate comparison with the corresponding *cobalti*-salt, which is completely isomorphous with it, the heteropolar binary axis of the crystals is also in this case adopted as *a*-axis.

To the well-developed pyramid *o*, which never fails and always gives good reflexes, the symbol  $\{111\}$  has been attributed, so that the ratio  $c:b$  is now exactly *half* the corresponding ratio of the *cobalti*-salt studied previously: there the symbol  $\{112\}$  was given to the form *o*.

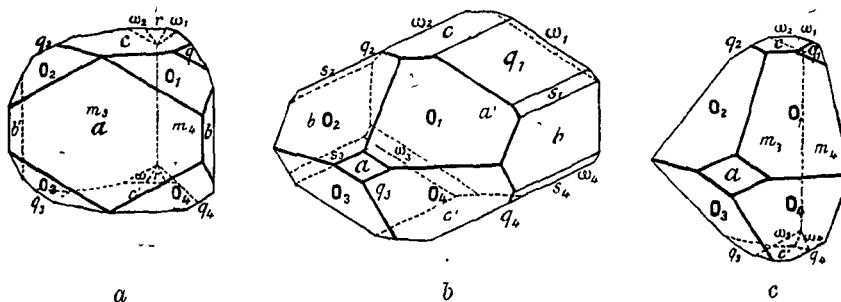


Fig. 8.

Racemic Tri-ethylenediamine-Rhodium-Nitrate.

*Rhombic-pyramidal.*

$$a:b:c = 0,7874:1:0,5606.$$

*Forms observed:*  $a = \{100\}$ , well-developed, occasionally predominant and always very lustrous;  $a' = \{100\}$ , mostly absent or extremely narrow, sometimes, however, very large and reflecting perfectly;  $o = \{111\}$ , large and lustrous;  $m = \{120\}$ , if present large and lustrous, but occasionally absent;  $c = \{001\}$ , well-developed and giving very sharp reflexes;  $\omega = \{111\}$ , never failing, but always much smaller than *o*;  $q = \{011\}$ , occasionally absent, in most cases, however, large and lustrous;  $s = \{021\}$ , much narrower than *q*, but giving good images;  $r = \{20.01\}$ , small and dull, ordinarily absent;  $b = \{010\}$ , always sharply reflecting, and sometimes equally large as *q* and *c*, but occasionally much smaller or totally absent;  $p = \{120\}$ , extremely small, only rarely present.

The colourless crystals always exhibit a distinctly hemimorphic shape; the polar axis is the  $a$ -axis. The substance possesses a strong tendency to crystallisation, but the various individuals are in general smaller than those of the corresponding *cobalti*-salt.

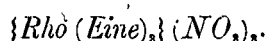
The external aspect is in most cases rather isometrical, but occasionally a slight elongation parallel to the direction of the  $a$ -axis could be stated.

Angles:	Observed:	Calculated:
$o:o = (111) : (\bar{1}\bar{1}1) = *$	$49^\circ \quad 51\frac{1}{3}'$	—
$a:o = (100) : (111) = *$	$58 \quad 9\frac{1}{2}$	—
$o:o = (111) : (1\bar{1}\bar{1}) =$	$95 \quad 36$	$95^\circ \quad 38'$
$b:o = (010) : (111) =$	$65 \quad 24$	$65 \quad 27\frac{1}{3}$
$o:q = (111) : (011) =$	$31 \quad 47$	$31 \quad 50\frac{1}{2}$
$c:o = (001) : (111) =$	$42 \quad 10$	$42 \quad 11$
$c:q = (001) : (011) =$	$29 \quad 10$	$29 \quad 16\frac{1}{2}$
$q:s = (011) : (021) =$	$19 \quad 10$	$19 \quad 0$
$s:b = (021) : (010) =$	$41 \quad 44$	$41 \quad 43\frac{1}{2}$
$\omega:q = (\bar{1}\bar{1}1) : (011) =$	$31 \quad 50$	$31 \quad 50\frac{1}{2}$
$c:\omega = (001) : (\bar{1}\bar{1}1) =$	$42 \quad 7$	$42 \quad 11$
$m:m = (\bar{1}20) : (\bar{1}20) =$	$115 \quad 16$	$115 \quad 10$
$a:m = (100) : (\bar{1}20) =$	$122 \quad 22\frac{1}{2}$	$122 \quad 25$
$c:r = (001) : (\bar{2}0.01) =$	$85 \quad 0$	$84 \quad 54$
$r:r = (\bar{2}0.01) : (\bar{2}0.01) =$	$9 \quad 56$	$10 \quad 12$
$o:m = (111) : (\bar{1}20) =$	$85 \quad 50$	$85 \quad 55$

No distinct cleavage was observed.

On  $\{100\}$  the optical extinction is parallel and perpendicular to the  $c$ -axis. The plane of the optical axes is  $\{010\}$ .

## § 12. LAEVOGYRATORY TRI-ETHYLENEDIAMINE-RHODIUM-NITRATE.



This compound was prepared from the laevogyrate *iodide* by means of *silver-nitrate*. It crystallises in beautiful, triangularly-shaped plates, or, in most cases, in crystals of the form reproduced in fig. 9.

The various individuals are distorted in most capricious ways, a fact which to no slight degree opposes their investigation.

*Rhombic-bisphenoidical.*

$$a : b : c = 0,8642 : 1 : 0,6049.$$

Forms observed:  $a = \{100\}$  and  $o = \{\bar{1}\bar{1}1\}$ , almost equally large;  $r = \{101\}$ , commonly present with only two faces;  $m = \{110\}$ ,

small but well reflecting;  $p = \{120\}$ , much smaller than  $m$ , and often totally absent. The shape of the crystals is that of plates parallel to  $\{100\}$ , or to two parallel faces of  $m$ . They are completely *isomorphous* with those of the *cobalti*-salt.

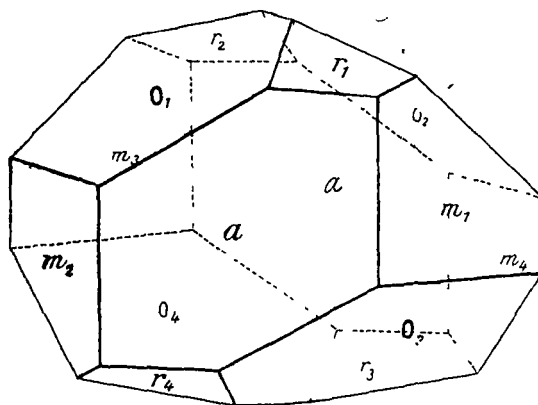


Fig. 9.  
Laevogyrate Tri ethylenediamine-Rhodium-Nitrate.

Angles:	Observed:	Calculated:
$a : m = (100) : (110) =^*$	$40^{\circ}50'$	—
$a : o = (100) : (\bar{1}\bar{1}1) =^*$	$59 \quad 5$	—
$a : r = (100) : (101) =$	$55 \quad 1$	$55^{\circ} \frac{1}{2}'$
$o : r = (\bar{1}\bar{1}1) : (101) =$	$26 \quad 13$	$26 \quad 21\frac{1}{3}$
$m : p = (110) : (120) =$	$19 \quad 11$	$19 \quad 7$
$o : m = (\bar{1}\bar{1}1) : (110) =$	$84 \quad 15$	$84 \quad 21$
$o : m = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}0) =$	$47 \quad 15$	$47 \quad 12\frac{1}{2}$
$o : o = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}\bar{1}) =$	$52 \quad 46$	$52 \quad 42\frac{1}{3}$
$o : p = (\bar{1}\bar{1}1) : (120) =$	$82 \quad 47$	$82 \quad 42\frac{1}{2}$
$a : p = (100) : (120) =$	$59 \quad 37$	$59 \quad 57$

No distinct cleavability could be found.

The plane of the optical axes is  $\{010\}$ ; in the corner of the image, one optical axis is visible under the microscope, when a plate parallel to  $m$  is used.

### § 13.

In the accompanying figure 10 the dispersion-curves of both the last mentioned salts have been reproduced. Their shape is absolutely different from that of the corresponding curves of the optically-active *cobalti*-salts.

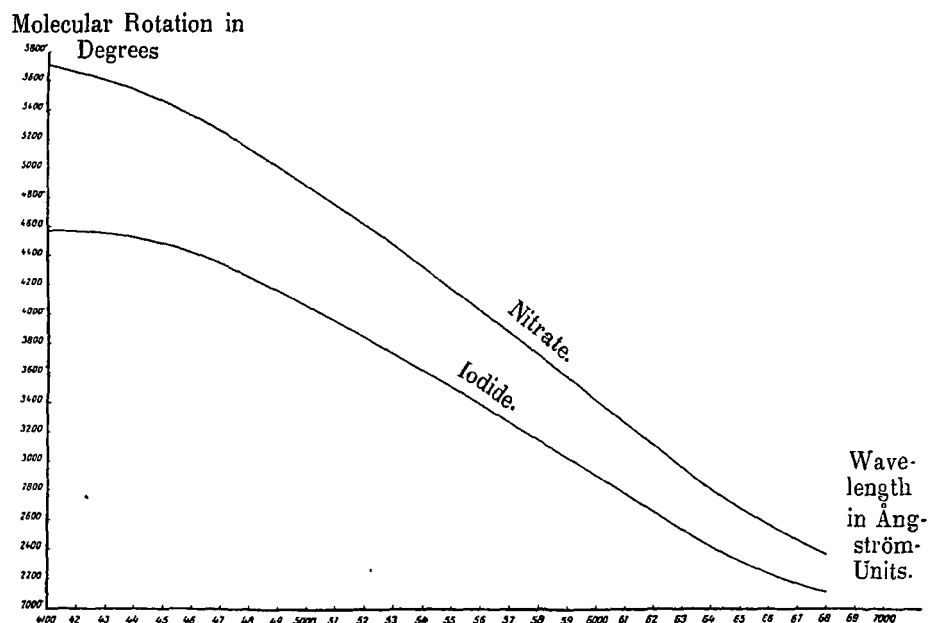


Fig 10. Molecular Rotation-Dispersion of Laevogyrate Triethylenediamine-Rhodium-Nitrate and -Iodide.

Rotation-Dispersion of Laevogyrate Tri-ethylenediamine-rhodium-nitrate.		
The liquid contained 3,372 grams of salt in 100 grams of the solution.		
Wave-length in ÅNGSTRÖM-Units :	Specific rotation $[\alpha]$ in Degrees :	Molecular rotation $[M]$ in Degrees :
6840	— 51,11	— 2397°
6660	— 55,44	— 2600
6520	— 56,50	— 2650
6380	— 60,55	— 2840
6260	— 63,55	— 2981
6140	— 67,99	— 3189
6030	— 71,21	— 3340
5890	— 76,75	— 3600
5800	— 78,81	— 3696
5700	— 82,37	— 3863
5605	— 85,77	— 4023
5510	— 89,48	— 4196
5420	— 91,70	— 4301
5340	— 93,92	— 4405
5260	— 97,18	— 4558
5180	— 98,66	— 4627
5100	— 100,59	— 4718
4945	— 105,63	— 4955
4780	— 110,45	— 5180
4650	— 114,22	— 5357
4480	— 117,27	— 5500
4310	— 119,85	— 5621

§ 14. In first instance it may be remarked in this connection, that the expected hemihedrism of the crystal-forms of the optically active *bromide* and *iodide* investigated, does *not* manifest itself in any distinct and convincing way, notwithstanding the enormous value of the optical rotation of these salts.

This fact is completely analogous to our previous experience in the case of the corresponding *cobalti*-salts. It proves once more that even if PASTEUR's principle be considered as principally correct, the chemical identity of the dissymmetrically arranged substitutes must be looked upon as a very unfavourable factor for the eventual manifestation of the hemihedrism predicted. These facts seem to sustain our view previously explained, according to which the dissymmetrical arrangement as such determines chiefly the size of the optical rotation of the molecule, while the chemical contrast between the different substitutes is the predominant factor for the manifestation of the crystallonomical enantiomorphism.

Moreover, WERNER<sup>1)</sup>, on the supposition, that analogously built dissymmetrical molecules always should combine with the same optically active radical into compounds showing *analogous solubility-relations*, concluded that the *laevogyrate Rho*-salts of the kind here described, and the *dextrogyrate Co*-salts would possess the same *stereometrical configuration*.

For from the *less soluble chloro-d-tartrates* of both series, the oppositely rotating *Rho*-, resp. *Co*-salts are set free, after the *d-tartaric acid* has been removed from them.

The Swiss scientist does not give sufficient and rational proof of the correctness of his starting hypothesis<sup>2)</sup>. On the contrary: the solubility of chemical compounds is a constitutive property of so highly a complicated nature, that there is every reason to doubt à priori the *general* correctness of the supposition mentioned above. Then, however, at the same time the value of WERNER's considerations, suggestive as they may be, has become appreciably diminished, in so far as they concern the specific influence of the central metal-atom on the direction of the optical rotation of the molecule.

As a counterpart of the views exposed by him, we therefore wish here to bring forward the following arguments which, in our opinion, appear to be founded on a firmer basis.

<sup>1)</sup> A. WERNER, loco cit Berl. Ber. 45. 1229 (1912). Bull. de la Soc. Chim. (1912), p. 21; G. URBAIN et A. SÉNÉCHAL, Introduction à l'Etude des Complexes, (1913), p. 174.

<sup>2)</sup> Some cases are mentioned in his paper: however, there is no certainty that really no inversion has occurred here during the experiment.



In the preceding paragraphs we were able to demonstrate :

1. that in analogously built, optically-*inactive* complex salts of trivalent *cobalt* and trivalent *rhodium*, the two metals will replace each other strictly *isomorphously*. This fact is in full agreement with what can be expected because of the place these elements occupy in the eighth group of the periodical system.

2. that in analogously built, optically-*active* complex salts of trivalent *rhodium* and *cobalt*, this *isomorphous* mutual substitution of the central atoms *remains*. This specific property of the metal-atoms obviously appears therefore *not* influenced by the special dissymmetry of the molecules, in which they are present.

Now we will suppose that the *dextro*-gyrate, and just in the same way the *laevo*-gyrate *tri-ethylenediamine-cobalti-chloride* is transformed into the corresponding *chloro-tartrates* by means of *silver-d-tartrate*. Of course the crystal-forms of both these compounds *d'd* and *l'd*, being no longer each other's mirror-images, will be *different* from each other. For among all properties of chemical molecules none is certainly so closely connected with their molecular configuration, as the crystal-form is. With respect to the identical *d-tartrate-radical* in the two compounds, it is therefore the two special configuration of the *d'*-, resp. *l'*-*tri-ethylenediamine-cobalti-radicals*, which determines the differences of crystal-form in the case of the two *chloro-d-tartrates* just mentioned.

If now, while completely preserving the existent stereometrical arrangement of the radicals round the central *Co*-atom, we think this last simply replaced by the *Rho*-atom which, according to what is mentioned sub 2°) in the above, will replace it in the way of a perfect *isomorphous* element, — then it will be evident that the two complex *Rho*-compounds thus obtained will be perfectly *isomorphous* with the two corresponding *Co*-salts just mentioned, and more particularly each of them with that *Co*-salt which possesses an analogous configuration of its radicals in space. This conclusion is compelling, quite independent of the other question concerning the special influence which this substitution eventually may have on the size and even on the sense of the optical rotation of the original molecule, or on its solubility. The *chloro-d-tartrates* of *Co*-an *Rho*-complexes with corresponding configuration therefore will exhibit perfectly *isomorphous* crystal-forms, independently of their specific optical properties or of the differences in their solubilities.

Also the number of molecules of water of crystallisation in the two *isomorphous* crystal-species will be exactly the same.

Experience now teaches us that the less soluble *tri-ethylene-*

*diamine-cobalti-chloro-tartrate* has *triclinic-pedial* symmetry <sup>1)</sup>, the less soluble *tri-ethylenediamine-rhodium-chloro-tartrate*, however, *monoclinic* and perhaps *sphenoidical* symmetry, *without the least analogy of the parameters existing between them*. No analogy of form whatever can be stated between the two kinds of *chloro-tartrates*; and in agreement with this lack of isomorphism, direct analysis showed that, while the *cobalti-salt* crystallises with 5 molecules  $H_2O$ , the less soluble *rhodium-salt* contains only 4 molecules of water of crystallisation, — the respective data in WERNER's paper being obviously erroneous. There can be therefore not the least doubt about the truth of the fact that we have *not* to deal here with isomorphous salts of corresponding constitution, but with quite different substances. In connection with what was said above, we are therefore compelled to conclude from these facts, that the complex *tri-ethylenediamine-rhodium-ion* present as a radical in the corresponding *chloro-d-tartrate*, has *not the same* configuration in space as the radical occurring in the less soluble *cobalti-chloro-d-tartrate*, but that it possesses on the contrary, precisely the antilogous stereometrical configuration in comparison with it. And because the *tri-ethylene-diamine-rhodium-iodide* set free from this *chloro-d-tartrate*, and all salts derived from it, appear to be *laevogyrotory*, it follows from this that the stereometrical configuration of optically-active *triethylenediamine-cobalti-*, and *rhodium-*ions of the same direction of rotation, must be the same also, — a fact which *a priori* might have appeared most probable.

The *d-cobalti-salts* must therefore possess *the same* arrangement of the radicals round their central metal-atom as the *d-rhodium-salts*, and the *l-cobalti-salts* the same as the *l-rhodium-salts*.

§ 15. With this conclusion at the same time WERNER's supposition of the strange, rather arbitrarily conjectured specific influence of the central *Rho*-atom, concerning *the total inversion of the direction of rotation* of the original dissymmetrical complex, needs to be given up. The analogously arranged dissymmetrical complexes containing *Cr*, *Co*, or *Rho*, must all exhibit *the same* direction of rotation, and only the absolute size of it may be different and varying in the way indicated by WERNER. This specific rotation is therefore evidently determined chiefly by the special configuration in space of the radicals placed round the central atom, and by the specific dissymmetry of

<sup>1)</sup> F. M. JAEGER, *Proceed. Kon. Acad. Amsterdam*, **18**, 54, 55. (1915).

that arrangement. Only in second instance the *mass* and the *chemical nature* of the central-atom seem to be of influence, and more especially in so far as concerns the changes of the size of the rotation, when the one kind of central atom is replaced by another isomorphous element.

It is worth remarking here, that the crystals of the optically-active *tri-ethylenediamine-cobalti-*, and *-rhodium-nitrate* here investigated, exhibit sphenoids of opposite algebraic signs in the case of active salts rotating in the same direction: the *laevo*-gyrate *cobalti*-salt manifest the *right*-handed sphenoid, while the *laevo*-gyrate *rhodium-nitrate* exhibits precisely the *left*-handed form.

On the surface of it, it may seem to be correct to consider this fact as an argument in favour of WERNER's view about the antilogous configurations of *cobalti*- and *rhodium*-salts of the same rotation-direction. But this conclusion must appear completely unjustified, as soon as the facts hitherto stated are taken into account, — scanty as these facts for the rest may be at this moment. The question: in how far is there any rational connection between the external appearance of form of a crystal and the stereometrical configuration of its molecules? — seems to be quite unanswerable at the present moment, because this external appearance of the crystal, depending on a great number of accidental circumstances during the process of crystallisation, is a very capricious and variable phenomenon. It is, for instance, well known, that the *K-*, ( $\Delta$ *NH*<sub>4</sub>)-, *Rb-*, and *Co-dextro-bitartrates*, all undoubtedly having the same stereometrical configuration (namely: of *d-tartaric acid*), may exhibit preferentially the forms {111} or {111} in a predominant way, if certain salts (e.g. *sodium-citrate*) be purposely added to their solutions, or if circumstances during the crystallisation be arbitrarily varied. In the case of the complex salts under consideration, which, moreover, appear to vary their outward appearance to a most intense degree under circumstances only slightly altered, such arguments, based only on this external form, can hardly have any value at all for judging the internal structure of their molecules, unless full certainty is obtained that the salts compared are deposited under exactly the same circumstances, as e.g. this may be assumed in cases, where racemoids are separated by so-called spontaneous crystallisation, the two kinds of crystals here being deposited simultaneously from the same mother-liquid.

At this moment the only conclusion can be, that the same configuration must be attributed to the *dextro*-, respectively *laevo*-gyrate complex-salts of *cobalt* and *rhodium*, when they exhibit a rotation of the same direction.

On comparing the molecular rotation of the *bromides*, *iodides* and *nitrates* of the two series:

<i>Tri-ethylenediamine-</i> <i>Cobalti-Bromide:</i> $[M]_D = \pm 6000^\circ$	<i>Tri-ethylenediamine-</i> <i>Cobalti-Iodide:</i> $[M]_D = \pm 6120^\circ$	<i>Tri-ethylenediamine-</i> <i>Cobalti-Nitrate:</i> $[M]_D = \pm 4600^\circ$
<i>Tri-ethylenediamine-</i> <i>Rhodium-Bromide:</i> $[M]_D = \pm 3500^\circ$	<i>Tri-ethylenediamine-</i> <i>Rhodium-Iodide:</i> $[M]_D = \pm 3020^\circ$	<i>Tri-ethylenediamine-</i> <i>Rhodium-Nitrate:</i> $[M]_D = \pm 3600^\circ$

we see that the *Co*-salts, besides exhibiting a much greater rotation-dispersion, also possess a much greater absolute rotation.

This fact will appear conceivable, if we bear in mind the very different chemical nature of the two isomorphous central atoms, and the rather appreciable difference in their atomic weights (59 and 103).

Some experiments on the properties of the analogous *Ir*-salts in this respect, are planned in this laboratory.

*Laboratory for Inorganic and Physical Chemistry*  
*of the University, Groningen, Holland.*