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# Mathematics. — "Remark on inner limiting sets". By Prof. L. E. J. BROUWER.

#### (Communicated in the meeting of April 23, 1915).

The notion of *inner limiting set* i.e. the set of all the points common to a series of sets of regions, was prepared by BOREL<sup>1</sup>), and fully developed by YOUNG<sup>2</sup>). The two principal theorems about this class of sets are the following:

1. An inner limiting set containing a component dense in itself, has the continuous potency.

2. A countable set containing no component dense in itself, is an inner limiting set.

The former theorem has been proved by Young, first for the linear domain, then for the space of n dimensions<sup>3</sup>). The latter theorem has been proved for the first time by HoBSON<sup>4</sup>). It is true that this theorem can be considered as a corollary of the following theorem enunciated somewhat before by Young<sup>5</sup>):

3. If Q be an arbitrary set of points, an inner limiting set exists containing besides Q only limiting points of the ultimate coherence  $\circ$ ) of Q;

but this theorem was deduced by YOUNG<sup>5</sup>) from the property: "Each of the successive adherences<sup>7</sup>) of a set of points consists entirely of points which are limiting points of every preceding adherence", and the proof given by YOUNG for this property is erroneous<sup>8</sup>), so that undoubtedly the priority for the proof of theorem 2 belongs to HOBSON.

We can, however, arrive at theorem 2 in a much simpler way

<sup>2</sup>) Leipziger Ber. 1903, p. 288; Proc. London M. S. (2) 3, p. 372.

<sup>1)</sup> Leçons sur la théorie des fonctions, p. 44.

<sup>&</sup>lt;sup>3</sup>) Leipziger Ber. 1903, p. 289-292; Proc. London M. S. (2) 3, p. 372-374. These proofs are referred to not quite exactly by SCHOENFLIES, Bericht über die Mengenlehre II, p. 81 and Entwickelung der Mengenlehre I, p. 356.

<sup>4)</sup> Proc. London M. S. (2) 2, p. 316-323.

<sup>&</sup>lt;sup>5</sup>) Proc. London M. S. (2) 1, p. 262-266.

<sup>6)</sup> YOUNG, Quarterly Journ of Math, vol. 35, p. 113.

<sup>7)</sup> CANTOR, Acta Mathematica 7, p. 110.

<sup>&</sup>lt;sup>8</sup>) Quarterly Journ. of Math., vol. 35, p. 115. The error is contained in the sentence (line 8-6 from the bottom): "Thus *P*, being a limiting point of every one of the derived coherences, is a limiting point of *F*". A correct proof of the property in question was communicated to me about two years ago by G. CHISHOLM YOUNG.

than HOBSON and YOUNG did, by means of the following ') proof of theorem 3, which is valid for the space of n dimensions:

For each positive integer v we describe round each point q of Q as centre with a radius smaller than  $\varepsilon$ ,  $(\lim \varepsilon = 0)$  a sphere which, if q is a point of the adherence  $Qc^{\beta}a$ , excludes all points of the derived set of  $Qc^{\beta}$ . In this way for each positive integer v a set of regions J, containing Q is determined.

The inner limiting set  $\mathfrak{D}(J_{\cdot})$  then possesses the property required. For, if p be a limiting point of Q not belonging to Q and not being a limiting point of the ultimate coherence of Q, a transfinite number  $\tau_p$ exists with the property that p is not a limiting point of  $Qc^{\tau_p}$ , but for any  $\alpha < \tau_p$  is a limiting point of  $Qc^{\alpha}$ . Then on one hand p is excluded by every sphere described round a point of  $\sum Qc^{\alpha}a$ , on the other hand a positive integer  $\sigma_p$  exists so that p is excluded by every sphere described for a  $v > \sigma_p$ , round a point of  $Qc^{\tau_p}$ . Hence p lies outside every J, for which  $v > \sigma_p$ , so that p cannot belong to  $\mathfrak{D}(J_{\tau})$ . Thus the theorem has been established.

# Chemistry. — "Investigations on PASTEUR'S Principle of the Relation between Moleculur and Physical Dissymmetry." II. By Prof. Dr. F. M. JAEGER. (Communicated by Prof. H. HAGA).

(Communicated in the meeting of April 23, 1915).

§ 1. In the following are reviewed the results of the crystallographical investigations upon which the conclusions explained in the previous paper<sup>2</sup>) are founded.

> I Racemic Luteo-Triethylenediamine-Cobaltbromide. Formula:  $\{Co(Aein)_3\}Br_3 + 3H_2O$ .

This compound was prepared by two methods: 1. Starting from *praseo-diethylenediamine-dichloro-cobaltichloride*:  $\{Co(Aein)_2 Cl_2\} Cl$ , by heating with ethylenediamine and precipitating with a concentrated solution of sodiumbromide; 2. By heating *purpureo-pentamine-*

<sup>2</sup>) Vid These Proceedings, March 1915.

Proceedings Royal Acad. Amsterdam. Vol. XVIII.

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<sup>&</sup>lt;sup>1</sup>) This proof was communicated about two years ago to SCHOENFLIES, who on p. 356 of his Entwickelung der Mengenlehre I, applies it to prove the following special case of theorem 2: "*Every component of a countable closed set is an inner limiting set*". Comp HOBSON, l. c. p. 320: "*Every reducible set is an inner limiting set*".

chlorocobaltichloride:  $\left\{ Co \frac{(NH_3)_5}{Cl} \right\} Cl_2$ , with three molecules of triethylenediamine for a considerable time, and precipitating the compound with sodiumbromide.

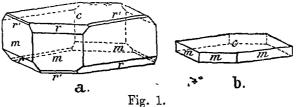
A. The salt prepared by the method indicated sub 1 is deposited from the yellow-brown solutions as hexagonal plates of red-brown or orange colour, or in the shape of hexagonal, short prisms. (fig  $.1\alpha$ and 1b).

Pseudo-ditrigonal-scalenoedrical, but probably really monoclinic a: c = 1: 0.6794.

The compound is almost perfectly isomorphous with the corresponding chloride; however the cleavage differs in the two salts.

Observed Forms:  $c = \{0001\}$ . most prominent and giving good – images;  $m = \{10\overline{1}0\}$ , often very well developed, shows however in most cases broken faces, giving multiple reflections;  $r = \{10\overline{1}1\}$ , sometimes small, but occasionally rather large;  $r' = \{10\overline{1}1\}$ , often absent, several times very narrow, and in rare cases as well developed as r; perhaps  $s = \{42\overline{6}3\}$ , occasionally visible as an extremely narrow blunting.

Angular Values :	Measured:	Calculated :
$r : c = (10\overline{1}1) : (0001)$	== *38° 7′	~
$r : m = (10\overline{1}1) : (10\overline{1}0)$	= 5150	51053'
$m:m = (10\overline{1}0): (01\overline{1}0)$	= 60 2	60 0
$c : s = (0001) : (42\overline{63})$	== ca. 540	54 9
$r : r = (10\overline{1}1) : (\overline{1}101)$	= -	64 38



Racemic Triethylenediamine-Cobaltibromide.

A perfect cleavage occurs parallel to {0001}. Plates perpendicular to the *c*-axis are however completely dark in no situation between crossed nicols, if the light is polarized parallel. Occasionally they appear to be composed of lamellae parallel to {0001}, like the wellknown mica-piles of REUSCH and MALLARD, as might also be proved perhaps by the often observed anomalies of the angular values.

The crystals are optically-uniaxial; the birefringence is of a negative character. They do not show a rotatory polarisation; their dichroism

the test to the

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is clearly visible: on  $\{10\overline{1}0\}$  for vibrations parallel to the *c*-axis orange-red, for those perpendicular to the former orange-yellow. The specific weight of the crystals was determined at 25° C. pycnometrically:  $d_{4^\circ}^{25^\circ} = 1.845$ ; the molecular volume<sup>1</sup>) is thus: 577.8, and the topical axes  $\chi: \omega = 10,9400: 7,4328$ .

B. The substance prepared from *purpureo-dichloro*-salt crystallised from its aqueous solution in the shape of hexagonal plates, which will commonly show not only c and m, but also r and r'. The optical behaviour and the angular values agree completely with those of the previously described salt. Further, we obtained the same modifications in separating the bromo-tartrate into its optically active forms as in the first case; also the d-bromo-tartrate was here identical with that obtained from the first salt. There cannot be any doubt, but that the two bromides are quite identical; the specific gravity of the last crystals also, being found at: 1.142 at  $25^{\circ}$  C., is in agreement with this supposition.

With the kind assistance of my colleague HAGA a beautiful RONTGENogram of these hexagonal plates was made. The stereographic projection of it is reproduced on Plate I, in A. It appears now, that there is no ditrigonal symmetry at all: the photo reveals only a single plane of symmetry, as if a mere monoclinic-domatic symmetry were present. For the present no other explanation can be given here, than the supposition of the crystral being only a pseudotrigonal complex of perhaps monoclinic lamellae; in every case the very perfect approximation of that complex to a real ditrigonal crystal is a quite remarkable fact; it remains yet very strange however, whyonly a single plane of symmetry will appear in this image.

# II. Dextrogyratory Luteo-Tricthylenediamine-Cobaltibromide. Formula: $\{Co(Aein)_s\} Br_s + 2 H_s O.$

The compound was obtained by the transformation of the racemic salt in aqueous solution into the corresponding *d-bromo-d-tartrate* by means of silver-*d*-tartrate and afterwards fractionated crystallisation. The *d-bromo-d-tartrate* - which is deposited first and whose beautiful crystals are also described in the following, is then treated with HBr to convert it into the dextrogyratory bromide; the same happened with the *l-bromo-d-tartrate*, which can be obtained only in the form of a colloidal mass. The rotation of the two salts in aqueous solutions appeared to be really equal but of opposite direction.

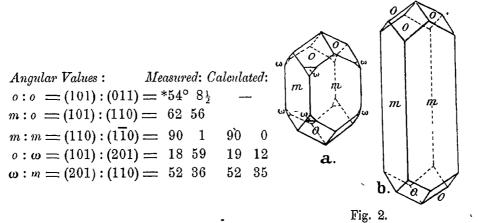
<sup>&</sup>lt;sup>1</sup>) In the following calculations we adopted 2M instead of M as the molecular weight of the racemic compounds. This latter one is undoubtedly also present still in the aqueous solutions of the salts.

Big crystals, occasionally a cc.m. in volume; they are brownish red, in most cases thick prisms with beautifully developed, lustrous faces. Commonly they are flattened parallel to two opposite faces of m; also the dodecahedrical crystals were observed, which are described in the case of the laevogyratory antipode.

#### Ditetragonal-bipyramidal.

## a:c=1:0.8399.

Observed Forms:  $m = \{110\}$ , in most cases predominant, sometimes giving multiple images;  $o = \{101\}$ , with great, lustrous faces, allowing very accurate measurements;  $\omega = \{201\}$ , well developed, but often absent. (fig. 2a and 2b).



Dextrogyratory Triethylenediamine-Cobaltibromide.

A distinct cleavage could not be stated.

On  $\{110\}$  the extinction is normal; the crystals are not appreciably dichroitic. They are uniaxial, with negative birefringence. They show a strong rotatory polarisation: a plate perpendicular to the optical axis appeared to be strongly dextrogyratory: about 25° or 30° for the transmitted orange-red light, and a thickness of 1 m.m. If a similarly directed plate of the laevogyratory salt is combined with it, one sees the spirals of *Airy* very distinctly like four dark beams, radiating from the centrum of the image into direction of motion of the hands of a clock, if the dextrogyratory plate is the upper-one of the two.

The specific weight of the crystrals was at  $25^{\circ}$  C.:  $d_{4^{\circ}} = 1.971$ ; the molecular volume is thus: 261.29, and the topical parameters are:

 $\chi: \psi: \omega = 6,7759: 6,7759: 5,6910.$ 

By means of a diluted solution of potassiumchlorate, finally corro-

sionfigures on  $\{110\}$  could be obtained, having the shape of kites or long hexagons; they appeared symmetrical with respect to a horizontal and to a vertical plane From this and the holohedrical development of the crystals, it must be concluded that they can *not* be considered to have tetragonal-trapezohedrical symmetry, but that they must be described as of ditetragonal-bipyramidal symmetry.

On the rotation in solution and its dispersion, the data of the previous paper can be consulted.

The Rontgenogram obtained of a plate perpendicular to the c-axis was too imperfect, to make a good reproduction possible. Thus on Plate I in B we have given its stereographical projection; it appears to possess all the symmetry-elements of a ditetragonal-bipyramidal crystal, and inter alia the four vertical symmetry-planes and the quaternary axis can be easily distinguished. In reality the photo for the laevogyratory salt, notwithstanding its imperfection, appeared to be *identical* with that of the dextrogyratory salt. In all cases studied up till now, we have found the RONTGENOgrams of the dextro- and laevogyratory crystals always identical, just as the theory of the phenomenon postulates: . so in the cases of quartz, cinnabar, etc. However we found in these investigations some quite remarkable facts, which are already partially described in these Proceedings (March 1915), and which can lead to a perhaps justifiable doubt about the correctness of the suppositions accepted hitherto about the explanation of the symmetry-properties of the RONTGENOgrams, notwithstanding the above-mentioned agreement of facts and theory in the case of the optically active crystals.

In any case it appeared *not* to be possible to prove in this way the presence of enantiomorphous forms.

All experiments made with the purpose of obtaining limiting crystalfaces, which could demonstrate the hemibedrical character of the crystals, either by crystallisation from neutral or alkaline or acid solutions, either by addition of other salts to the aqueous solutions, — were without any other result, than that of *always* giving holohedrical crystal-forms. In connection with the above-mentioned experience, we have *no* reason to suppose the occurrence of hemihedrical crystals in this case.

The optical rotation of the crystals must thus be ascribed wholly to the optically active molecules themselves, which here build up the holohedrical molecular configuration of the crystals. In the same way, as e.g. sodiumchlorate is a salt, whose *inactive* molecules are arranged in a hemihedrical space-lattice, which causes the rotatory power of the crystals, — in the same way we must suppose the reverse case to be present here, where a holohedrical molecular structure will thus be built up by optically active molecules.

*III.* In connection with the foregoing description of the dextrogyratory antipode, the crystal forms of the corresponding bromoand *chlorotartrates*, from which the active compound could be prepared, may here be described in detail also.

The dd'-luteo-triethylenediamine-cobaltichlorotartrate, as well as the corresponding dd'-luteo-triethylenediamine-cobaltibromotartrate, crystallise from the solutions of the racemic chloride, resp. bromide, after being mixed with silver-d-tartrate-solutions, in the shape of hard, very beautiful, translucid and commonly big crystals. If eliminated from the original solution, this last will solidify, after having been again concentrated and some more of the abové-mentioned crystals having been separated, into a brownish-red jelly, which for the greater part represents the dl'-bromotartrate, and which after treatment with HBr, will give the laevogyratory antipode, besides some of the racemic compound. After a considerable time the jelly of the dl'-bromotartrate often gradually transforms into a cryptocrystalline mass.

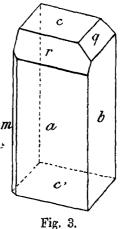
a. dd'-Luteo-Triethylenediamine-Cobaltichlorotartrate.

Formula: 
$$\{Co(Aein)_{s}\} \stackrel{Cl}{(C_{4}O_{s}H_{4})}$$

Big lustrous, brownish-yellow crystals (fig. 3), which commonly have the aspect of oblique parallelopipeda.

Triclinic-pedial. a:b:c = 0.6211:1:0.6521  $A = 103^{\circ} 42^{1}/_{2}' \qquad a = 102^{\circ} 20'$   $B = 102^{\circ} 46' \qquad \beta \doteq 101^{\circ} 16'$   $C = 98^{\circ} 1^{1}/_{2}' \qquad \gamma = 95^{\circ} 16^{2}/_{2}'$ 

Observed Forms:  $a = \{100\}$  and  $a' = \{\overline{1}00\}$ , large and lustrous;  $b = \{010\}$ ,  $b' = \{0\overline{1}0\}$ ,  $c = \{001\}$ and  $c' = \{00\overline{1}\}$ , equally large and well reflecting;  $r = \{101\}$ , well developed;  $q = \{011\}$ , about as large as r;  $m = \{2\overline{3}0\}$ , only very narrow, and often totally absent. The angular values oscillate,



as in the case of the bromotartrate, not unappreciably : deviations of  $0^{\circ}30'$  to  $1^{\circ}$  are not seldom dd'.Triethylenediaminefound with different individuals. A distinct Cobaltichlorotartrate. cleavage was not found.

Angular Values:	Obser	ved:	Cal	culated :
a:b = (100): (010) =	*81°	$58\frac{1}{2}$		
b:c = (010):(001) =	*76 ·	$17\frac{1}{3}$		_
a:c = (100):(001) =	*77	14		-
a:r = (100): (101) =	*38	11		-
q:c = (011):(001) =	*28	26		-
q:b = (011):(010) =	47	$50\frac{1}{2}$	47°	$50\frac{1}{2}'$
r: c = (101): (001) =	39	3	39	3
$a:m = (100): (2\overline{3}0) =$	<b>4</b> 6	59 <u>‡</u>	<b>46</b>	49

A distinct dichroism was not observed. On all faces the extinction was oblique, but the extinction-angle on the prism-faces was only small with respect to the direction of the *c*-axis, — which is in agreement with the evident approximation to monoclinic symmetry, this last one can be easily seen, if the forms a and b are taken as  $\{110\}$ , resp.  $\{110\}$ , while *c* remains  $\{001\}$ .

#### b. dd'-Luteo-Triethylenediamine-Cobaltibromotartrate.

# Formula: $\{Co(Aein)_{s}\} \stackrel{Br}{(C_{4}O_{5}H_{4})}$

Big, very lustrous, perfectly transparent crystals (fig. 4), which are wholly analogous to those of the corresponding chlorotartrate. The angular values oscillate here still a little more than in the preceding case; but undoubtedly the crystals are completely isomorphous with the above-mentioned ones.

Triclinic-pedial.

a:b:c = 0.6208:1:0.6528. $a = 102^{\circ} 50^{2}/s'$  $A = 104^{\circ} 8'$  $\beta = 100^{\circ} 35'$  $B = 102^{\circ} 7'$  $\gamma = 95^{\circ} 14'$  $C = 97^{\circ} 55'$ 

Observed forms:  $b = \{010\}$  and  $b' = \{0\overline{10}\}$  large and lustrous;  $a = \{100\}$  and  $a' = \{\overline{100}\}, c = \{001\}$ and  $c' = \{00\overline{1}\}$ , all about equally well developed and giving good images;  $r = \{101\}$ , well developed and lustrous;  $r' = \{\overline{101}\}$  commonly absent;  $o = \{\overline{113}\}$  small, but allowing exact measurements;  $o' = \{03\overline{2}\}$  narrow and somewhat dull. The angular values oscillate with different individuals not unappreciably, with differences of about 1°.

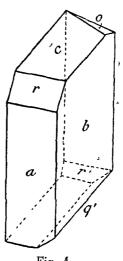


Fig. 4. dd'-Triethylenediamine-Cobaltibromotartrate.

Angular Values :	M easured:	Calculated :
a:b=(100):(010)	$=*82^{\circ}5$	—
b: c = (010): (001)	=*7552	
a:c = (100):(001)	= *7753	
$o: b = (\overline{1}13): (010)$	=*6656	~ <u> </u>
c: r = (001): (101)	= *39 37	-
a:r = (100): (101)	= 38 23	38°16′
$o: c = (\overline{1}13): (001)$	= 21 39	21 7
$o: a = (\overline{1}13): (100)$	= 84 46	84 42
$c': \hat{q} = (00\overline{1}): (03\overline{2})$	= 50 38	$50 \ 49\frac{1}{2}$

No distinct cleavage could be stated.

On all faces the extinction-angles are other than rectangles; the crystals have a sherry-like colour, and are not distinctly dichroitic.

IV. Laevogyratory Luteo-Triethylenediamine-Cobaltibromide.

Formula:  $\{Co(Aein)_{s}\}Br_{s}+2H_{s}O.$ 

Big, brownish-red, commonly rhombic dodecahedrically shaped, very lustrous crystals, which make very accurate measurements possible.

# Ditetragonal-bipyramidal.

$$a:c = 1:0.8399.$$

Observed Forms:  $m = \{110\}$ , usually as largely developed as o, giving the crystals thereby the aspect of rhombicdodecahedrons (fig. 5); sometimes however m is strongly predominant either with all its faces or with two parallel ones only, in such a way that the crystals get a column-shaped or tabular aspect. Further:  $o = \{101\}$ , big and lustrous; rarely:  $\omega = \{201\}$ , small but very easily measurable. The faces of  $\{110\}$  sometimes give multiple images.

Angular Values :	Observed:	Calculated:
o: o = (101): (011) =	:*54° 6′	
o: m = (101): (110) =	62 55	62° 57'
$o: o = (101): (\overline{101}) =$	80 7	80 3 <del>1</del>
$\omega: o = (201): (101) =$	19 8	$19 \ 12\frac{1}{3}$
$\omega: m = (201): (110) =$	52 30	$52 \ 35$

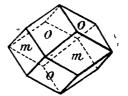


Fig. 5. Laevogyratory Luteo-Triethylenediamine-Co baltibromide.

No distinct cleavage was found.

With respect to the symmetry of the crystals the same can be said as in the case of the dextrogyratory compound. Corrosion-experiments on the faces {101} and {110} by means of water, mixtures of water and alcohol, etc. in most case gave irregularly defined corrosion-figures, which had the character of elevations.

The crystals are uniaxial with negative birefringence; like those of the dextrogyratory component they show a strong circular polarisation in the direction of the optical axis, which for a plate of about 1 mm. thickness appeared to be equal and directed oppositely to that of the dextrogyratory crystals.

On superposition of a dextro- and laevogyratory crystal, the latter being the upper, the AIRY-spirals are nicely seen, with their direction of rotation just opposite to that mentioned in the description of the dextrogy ratory crystals.

The specific gravity of the crystals was pycnometrically determined and found to be  $d\frac{25^{\circ}}{4^{\circ}} = 1.972$ ; the molecular volume thus is: 261.19, and the topical parameters are :  $\chi : \psi : \omega = = 6.7589 : 5.6767$ .

# V. Racemic Luteo-Triethylenediamine-Cobaltinitrate.

#### Formula : $\{Co(Aein)_s\}(NO_s)_s$

This compound was prepared by treatment of the racemic bromide in aqueous solution with a warm solution of the quantity of silvernitrate calculated. The solution separated from the precipitated silver-bromide was sufficiently concentrated on the waterbath; at roomtemperature dark red or brownish red, big, hemimorphic crystals will be separated.

In general the parameters and angular values appear to be the same as previously published (Z. f. Kryst. **39**. 548. (1904). The figure reproduced there however must now be changed, because the hemimorphy is now clearly demonstrated; further a wrong value of the angle o:q was introduced in the description, evidently by an accidental interchange of the symbols  $\{021\}$  and  $\{120\}$ .<sup>1</sup>) For the purpose of comparison of the calculated parameters with those of the optically active forms, we have, contrary to the common usage the polar binary axis as the *a*-axis.

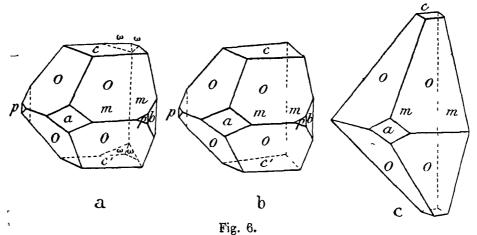
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<sup>&</sup>lt;sup>1</sup>) These incorrect data are also reproduced in GROTH's Chemische Krystallographie, II. 140. (1908); they must be corrected there by the numbers given here.

# Rhombic-pyramidal.

$$a:b:c = 0.8079:1:1,1279.$$

Observed forms:  $o = \{112\}$ , large and lustrous;  $a = \{100\}$ , smaller, but also giving beautiful images;  $m = \{\overline{1}20\}$ , almost equally well developed as o, sometimes even with yet larger faces;  $p = \{120\}$ , appreciably smaller than m, but very lustrous;  $b = \{010\}$  narrow;  $c = \{001\}$  commonly absent, but if present well developed and giving good images;  $\omega = \{\overline{1}12\}$ , with very small but lustrous faces;  $a' = \{\overline{1}00\}$ almost in every case absent, but sometimes present as a very narrow blunting of the intersection  $(120): (\overline{1}20)$ . The crystals possess commonly a very peculiar irregularly-tetrahedrical habit, with prominent faces of o and m.



Racemic Triethylenediamine-Cobaltinitrate.

Angular Values :	Observ	ed:	Calcu	ilated :
a:o = (100): (112) =	= *58°	42'	-	-
o: o = (112): (112) =	= *49	<b>3</b> 8	-	
$o: o = (112): (11\overline{2}) =$	= 96	11	96°	12'
$o: m = (1\overline{1}2): (\overline{1}\overline{2}0) =$	= 85	18	85	13
o: p = (112): (120) =	= 50	53	50	56
$b: m = (010): (\overline{120}) =$	= 31	53	31	<b>45</b>
a:p = (100): (120) =	= 58	10	58	15
p:p = (120): (120) =	= 116	<b>20</b>	116	30
m: m = (120): (120) =	= 116	17	116	30
$c: \omega = (001) : (112) =$	= 41	<b>54</b>	41	<b>54</b>
$\omega:\omega=(\overline{1}\overline{1}2):(\overline{1}\overline{1}2)=$	= 49	36	49	38

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A distinct cleavage was not found.

On [100] and [001] diagonal extinction.

The specific gravity of the crystals was determined at 25° C. pycnome- $25^{\circ}$ 

trically to be:  $d\frac{25^{\circ}}{4^{\circ}} = 1.709$ ; the molecular volume is thus 497.64.

Topical parameters:  $\chi : \psi : \omega = 6,6037 : 8,1740 : 9.2194$ .

The compound does not change the direction of the plane of polarisation of the incident light.

# VI. Laevogyratory Luteo-Triethylenediamine-Cobalti-nitrate.

# Formula : $\{Co(Aein)_{s}\}(NO_{s})_{s}$ .

The compound was prepared from the bromide by means of silvernitrate in small excess and at lower temperature; after separating from the silverbromide, the solution obtained was concentrated on the waterbath. From this solution, which thus contained a slight excess of silvernitrate, big, dark-red crystals were obtained, which gave splendid images, and made very accurate measurements possible.

The crystals, which have the habit of thick, trapezohedrically or pentagonally bounded plates, are usually developed parallel to opposite faces of the prism. They are extraordinarily rich in faces, and geometrically very well built; commonly the faces of the forms 011}, {021}, {211} and {010}, are only partially present, a fact, which in connection with the peculiar distortion of the crystals, often impedes appreciably the exact crystallographical analyses of them.

#### Rhombic-bisphenoidic.

#### a:b:c = 0.8647:1:0,5983.

Observed Forms:  $a = \{100\}$ , well developed and giving beautiful images;  $m = \{110\}$ ; larger than a, giving good reflections;  $r = \{101\}$ , somewhat smaller than m, but in most cases equally well developed;  $o = \{111\}$ , giving good images and relatively large;  $s = \{211\}$  narrower, but reflecting well;  $q = \{011\}$  and  $p = \{021\}$ , usually with only half the number of their faces present, but developed rather largely;  $b = \{010\}$ , narrower than a and reflecting well.



Angular	Values :	0	bserve	d: (	Calcul	ated :
a:m=(1	00) : (110)	=	*40°	51'		
a : o = (1	00):(111)	=	*59	18		-
o : m = (1	11):(110)	=	47	<b>28</b>	$47^{\circ}$	33'
m:m=(1	10):(110)	=	98	18	98	18
r:m = (1	01):(110)	=	64	$30\frac{1}{2}$	64	$30\frac{1}{2}$
o : o = (1	11):(111)	=	84	58	84	<b>54</b>
b : s = (0	10):(211)	=	70	41	70	4 <b>1</b>
$r : q = (\overline{1})$	01):(011)	=	45	16	45	7
r : o = (1	01):(111)	=	26	22	26	12
$o : b = (\overline{1}$	11):(010)	=	63	43	63	48
b : m = (0	10):(110)	=	49	4	49	9
a : r = (1	00):(101)	=	55	15	55	19
m: q = (1	10):(011)	=	70	21	70	23
m: p = (1	10):(021)	=	59	43	59	$52\frac{1}{2}$
p : o = (0	21):(111)	=	35	43	35	43
o:m=(1	11):(110)	==	84	33	84	$24\frac{1}{2}$
r : s = (1	01):(211)	=	27	13	27	$9\frac{1}{2}$
$m: s = (\overline{1}$	10):(211)	=	37	17	37	<b>21</b>
r : p = (1)	01):(021)	=	58	20	58	$10\frac{1}{2}$
q : p = (0	11) : (021)	=	19	14	19	13
a : s = (1)	00):(211)	-	40	4	40	$6\frac{1}{2}$
q : s = (0	$1\overline{1}$ : (2   $\overline{1}$ )	=	49	56	49	$53\frac{1}{2}$
q : o = (0	11):(111)	=	30	<b>4</b> 8	30	42
o : s = (1	11):(211)		19	15	19	$11\frac{1}{2}$
b : q = (0	10):(01 <b>1</b> )	=	59	4	59	$6\frac{1}{2}$
b : p = (0	10):(021)	==	39	58	39	53

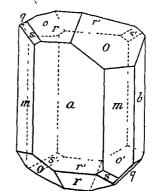


Fig. 7. Laevagyratory Triethylenediamine-Cobaltinitrate.

A distinct cleavage was not observed.

On {100} and {010}, also on {101} and {110} everywhere a normal extinction was found. The crystals are not appreciably dichroitic.

The specific gravity of the crystals at 25° C was:  $d\frac{25^{\circ}}{4^{\circ}} = 1.729$ ; the molecular volume is thus: 245.91. Topical parameters:  $\chi: \psi: \omega = 6.7486: 7.8046: 4.6695.$ 

# VII. Dextrogyratory Luteo-Triethylenediamine-Cobaltinitrate,

# Formula: $\{Co(Aein)_{s}\}(NO_{s})_{s}$ .

This compound was prepared in perfectly analogous way to the left-handed isomeride. From its aqueous solutions it crystallises as dark red, very large crystals with rectangular outlines. They are also very beautifully developed and give sharp images; the habit as well as the limiting planes are quite analogous to those of the laevogyratory component, but the crystals were in general not so strangely distorted, and they had somewhat smaller dimensions. They are the complete mirror-images of the crystals previously described.

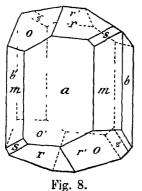
#### Rhombic--bisphenoidic.

# a:b:c = 0.8652:1:0.6009.

Observed Forms:  $a = \{100\}$  and  $m = \{110\}$ , both reflecting very well; m is somewhat more largely developed than a, and the crystals usually appear flattened parallel to two opposite faces of  $\{110\}$ . Further-on:  $r = \{101\}$ , well developed, and like  $o = \{111\}$ , giving very sharp images';  $s = \{211\}$ , small and showing in most cases only two faces;  $q = \{011\}$ , very small;  $p = \{120\}$  and  $b = \{010\}$ , extremely narrow and reflecting badly, often absent (fig. 8).

Angular Values:	Obser	ved :	Calcul	ated :
a : m = (100) : (1)	$(110) = *40^{\circ}$	52'		-
o:m=(111):(111)	(110) = *47	26		-
a : o = (100) : (100)	111) = 59	18	59°	14'
r : m = (101) : (1)	(110) = 64	31	64	$26\frac{1}{2}$
a : r = (100) : (1)	101) = 55	14	55	13
$o:r = (1\overline{1}1): (1\overline{1}1)$	101) = 26	32	<b>26</b>	<b>25</b>
m:m=(110):(1)	$1\overline{1}0) = 98$	14	98	12
r : r = (101) : (1)	(01) = 69	31	69	34
b : s = (010) : (2)	(211) = 70	37	70	$39\frac{1}{2}$
o: o = (1,1): (1,1)	111) = 85	8	83	5
$m:q = (1\overline{1}0):(0$	(01) = 70	16	70	$13\frac{1}{2}$
$r : q = (1 \lor \overline{1}) : (0$	(11) = 45	<b>20</b>	<b>45</b>	7
m:p = (110): (1)	120) = 18	55	19	$6\frac{1}{2}$
b: p = (010): (1)	120) = 30	0	30	$1\frac{1}{2}$
b : m = (0   0) : (1)	110) == 49	4	49	8
b : o = (0, 10) : (1)	$(\bar{1}1) = 63$	40	63	44

Topical parameters:  $\chi: \psi: \omega = 6,7467:7,:7979:4,6856.$ 



Dextrogyratory

A distinct cleavage was not observed. On  $\{100\}$ ,  $\{110\}$  and  $\{101\}$  the extinction is normal; the crystals are not distinctly dichroitic The plane of the optical axes is {001}; probably the *b*-axis is first bisectrix. The apparent axial angle is great, the dispersion has no exceptional value; round the a-axis it is q > v, with a negative character of the birefringence.

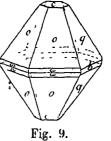
The specific weight of the crystals at 25° C. was determined at  $d \frac{25^{\circ}}{4^{\circ}} = 1,725$ ; the mole-Triethylenediamine-Cobaltinitrate cular volume consequently is 246,51.

#### VIII. Racemic Luteo-Triethylenediamine-Cobalti-iodide.

#### Formula: $\{Co(Aein)_3\}J_3 + 1H_2O$

The compound was prepared from the corresponding bromide by double decomposition with a solution of potassium-iodide; the precipitate was washed and recrystallised from warm water. On slow evaporation of the saturated solution, the small crystals can grow to fairly big individuals.

Splendid, dark-red to red-brown, very lustrous and clear crystals of octahedrical habit. The angular values of the different individuals may differ about 20'; every crystal as a whole however is geometrically very well built.



Racemic Triethylenediamine-Cobalti-iodide.

### Rhombic-bipyramidal.

$$a:b:c=0,8700:|:1.7399.$$

The crystals may be considered as pseudo-tetragonal, if the b-axis is chosen as the pseudo-quaternary axis.

Observed Forms:  $o = \{112\}$ , and  $q = \{021\}$ , about equally well developed; the faces of q are sometimes a little smaller than those of o, but both give very sharp images. Furthermore  $c = \{001\}$ , much smaller but giving good reflections;  $w = \{111\}$ , very narrow and somewhat dull, but quite measurable;  $b = \{010\}$ , extremely narrow and reflecting badly;  $x = \{101\}$ , rare and almost imperceptible.

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Angular values:	Observed :	Calculated:	
$o: o = (112): (1\overline{1}2) =$	*63° 12'		
c:q = (001):(021) =	*73 58	—	
c: o = (001): (112) =	$53 \ 3$	52° 58'	
o: w = (112): (111) =	16 11	162 2	-
$w: w = (111): (11\overline{1}) =$	$41 \ 35$	41 20	
$q:q = (021): (0\overline{2}1) =$	32 $4$	32 4	
q:b = (021):(010) =	$16 \ 2$	$16 \ 2$	
o:q = (112):(021) =	48 1	47 56	
c: x := (001) : (101) = c	irca 45 —	44 59 <u>}</u>	
$x: x = (101): (10\overline{1}) =$	89 52	90 1	

A distinct cleavage could not be observed.

On  $\{001\}$  diagonal extinction: the crystals are not perceptibly dichroitic. The plane of the optical axis is  $\{010\}$ ; the *c*-axis is first bisectrix. The apparent optical angle is very small.

The specific gravity of the crystals at  $25^{\circ}$  C. was pycnometrically determined  $d_{4^{\circ}}^{25^{\circ}} = 2.270$ ; the molecular volume is thus: 562.10.

Topical parameters:  $\chi : \psi : \omega = 6.2532 : 7.1877 : 12.5070.$ 

# 1X. Dextrogyratory Luteo-Triethylenediamine-Cobalti-iodide. Formula: $\{Co(Aein)_{s}\}J_{s} + 1H_{s}O.$

This compound was prepared by the precipitation of a solution of the dextrogyratory bromide with a concentrated solution of potassium-iodide; the precipitate was washed out and recrystallised from warm water. Analysis showed, that the compound, just like the racemic one, crystallizes with 1 molecule of water.

Long, dark-red, in transmitted light, blood-red needles, with lustrous faces. All faces of the prism-zone, with the exception of those of the forms {100} and {010}, are vertically striated; the vertical zone furthermore shows many vicinal forms, which make it often difficult, to find the exact angular values. (fig. 10).

# Rhombic-bipyramidal.

4

# a:b:c=0.8276:1:0.7386.

. Observed Forms:  $m = \{340\}$ , the largest of all prism-faces, giving like all prismatic faces, multiple reflections and diffraction-images;  $b = \{010\}$ , and  $a = \{100\}$ , somewhat narrower, but giving sharp reflections;  $p = \{120\}$  and  $s = \{3.16.0\}$ , both narrower than a, with s in most cases again smaller than p;  $q = \{011\}$ , well developed, but with rather appreciably oscillating angular values;  $r = \{102\}$ ,

giving very sharp reflections and easily measurable; ;  $t = \{104\}$  and  $\sigma = \{101\}$ , small but distinctly reflecting,  $w = \{071\}$ , very small and dull.

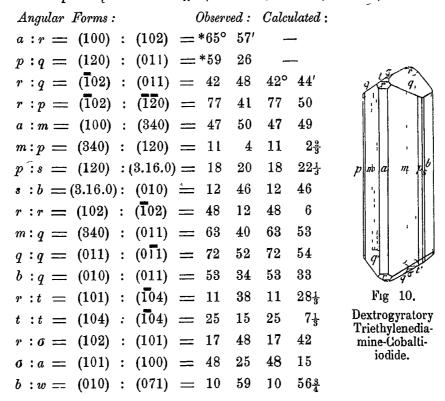
The habit of the crystals is elongated parallel to the c-axis.

A distinct cleavage was not observed.

On all faces of the vertical zone a normal extinction is found; no appreciable dichroism. The plane of the optical axes is  $\{001\}$ , with the *b*-axis as first bisectrix. The apparent axial angle is very small; the dispersion is strong  $\cdot \varrho < r$ . The birefringence is positive.

The specific gravity of the crystals at  $25^{\circ}$  C. was:  $d_{4^{\circ}}^{25^{\circ}} = 2.289$ ; the molecular-volume is thus  $\cdot 278,72$ 

*Topical parameters* :  $\chi : \psi : \omega = 6,3699 : 7,6968 : 5,6849$ .



On  $\{100\}$  we obtained with mixtures of alcohol and water very long, acute, hexagonal corrosion-figures and irregularly bordered rectangular elevations arranged in long rows. On the other hand we obtained on the faces of the prism triangular and trapeziumshaped corrosion-figures, which proved beyond doubt the presence of a. horizontal symmetry-plane, parallel to (//{001}).

The RONTGENOGRAM of a plate parallel to // {001} was very irregular and rudimentary, very probably however at least one single symmetry-plane might be present.

# X. Laevogyratory Luteo-Triethylenediamine-Cobalti-iodide.

# Formula: $\{Co(Aein)_{s}\}J_{1} + 1H_{2}O$ .

This antipode was prepared in a quite analogous way to that indicated in the case of the dextrogyratory component, and recrystallised from warm water. The crystals also contain, according to analysis, 1 molecule of water of crystallisation. They may grow to considerable size: one individual had a volume of more than 0.5 ccm.

Flat, dark-red to blood-red crystals, with lustrous faces, which give multiple reflections however, especially in the prism-zone

Observed Forms:  $p = \{120\}$ , large, but giving multiple images;  $q = \{011\}$ , also largely developed, and better reflecting than p,  $b = \{010\}$ , very lustrous and well reflecting;  $r = \{102\}$ . small, but very lustrous and well measurable,  $m = \{340\}$ , very narrow;  $\sigma = \{101\}$ , very small, and often absent;  $a = \{100\}$ , extremely narrow. The habit is somewhat elongated with respect to the c-axis. (fig. 11).

# Rhombic-bipyramidal.

$$a: b \cdot c = 0.8256: 1: 0.7395.$$

	Angular	Values :	Observe	ed:	Calcul	lated:	The second se
			0) == *31°		_	_	4
,	q:q =	(011):(01	1) == *72	58		-	
'			1) = 53		53°	31'	Parspo
	a:p =	(109) : (12	0) = 58	4 }	58	48	9.
	r:r =	(102) : (10	2) = 48	10	<b>4</b> 8	15 <del>]</del>	9
	$r: \sigma =$	(102) : (10	1) = 17	52	17	$43\frac{1}{3}$	
	p:q =	(120) : (01)	1) = 59	22	59	26	Fig. 11. Laevogyratory
	m:p = 0	(340) : (12)	() = 11	10	10	57	Triethylenediamine Cobalti-iodide.
							Conditi-ioulue,

No distinct cleavage was observed; one parallel to {001} may perhaps be supposed.

The optical orientation is the same as in the case of the dextrogyratory compound.

The specific gravity of the crystals at 25° C is:  $d \frac{25^{\circ}}{4^{\circ}} = 2.288 \cdot \text{the}$  molecular volume is thus  $\cdot$  278.84.

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#### *Topical parameter* : $\chi : \psi : \omega = 6.3580 : 7,7010 : 5.6950$ .

With cold water we obtained on {010} elongated, commonly irregularly shaped corrosion-figures. They seem to be symmetrical with respect to {100}, but perfect certainty could not be procured, notwithstanding many attempts made for this purpose.

#### XI. Racemic Luteo-Triethylenedumine-Cobalti-rhodanide.

#### Formula : $\{Co(Aein)_{s}\}(CNS)_{s}$ .

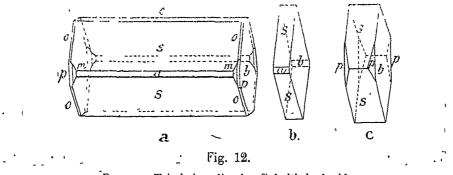
The compound was prepared by double composition of the racemic bromide with a concentrated solution of potassiumrhodanide, washing the yellow precipitate, and recrystallising from hot water. The crystals grow to rather large individuals in the solution, saturated at room-temperature and have a flat, spindle-like shape. According to analysis, they are *anhydrous*.

Red-yellow or yellow-brown, flat, spindle-shaped, acute, often distorted crystals, which are easily measurable.

# Rhombic-bipyramidal.

# a:b:c = 0.8405:1:0.8130.

Observed Forms:  $s = \{201\}$ , prominent and reflecting well, but sometimes giving multiple images;  $b = \{010\}$  and  $p = \{120\}$ , giving extremely sharp reflections, and thus exactly measurable;  $m = \{110\}$ , lustrous, somewhat smaller than p;  $o = \{211\}$  and  $x = \{321\}$ , as narrow bluntings. The crystals are elongated parallel to the *b*-axis, in several cases also parallel the *a*-xis; in the last mentioned case the habit of the small crystals is the acute, spindle-like one already described. (fig. 12 *a*, *b* and *c*)



Racemic Triethylenediamine-Cobalti-rhodanide,

....

Angular Values:	Observ	ed:	Colou	lated :
s: c = (201): (001) =	*62°	40'	-	
b: p = (010): (120) =	: *30	45	-	
s: a = (201): (100) =	: 27	<b>20</b>	27°	20'
p: a = (120): (100) =	: 59	15	59	15
p: m = (120): (110) =	: 19	<b>5</b>	19	12;
p: s = (120): (201) =	62	52	$\overline{62}$	59
p: x = (120): (321) =	: 33	55	33	57
a: s = (321): (201) =	29	16	29	<b>2</b>
b: o = (010): (211 =	69	19	69	32
o: s = (211): (201) =	20	41	<b>20</b>	28

67

A distinct cleavage was not observed.

11

In the zone of the ortho-diagonal the extinction is everywhere normal; the crystals are not distinctly dichroitic. On {120} triangular corrosionfigures were obtained. which were in agreement with the symmetry mentioned.

The specific weight of the crystals was at 25° C. pycnometrically determined to be:  $d_{10}^{250} = 1.511$ ; the molecular volume is: 547.24.

*Topical parameters*:  $\chi : \psi : \omega = 7.8053 : 9.2864 : 7.5499$ .

XII. Dextrogyratory Luteo-Triethylenediamine-Cobalti-rhodanide.

# Formula: $\{Co(Aein)_{s}\}(CNS)_{s}$ .

The active compounds were prepared from the dextro- or laevogyratory bromides in a quite analogous way, as indicated by the racemic rhodanide. Analysis proved that these optically active modifications crystallise *without* water of crystallisation.

Beantifully formed, orange to blood-red, splendidly reflecting, quadrangular thick plates or flattened, shortprismatic, small crystals, which make accurate measurements quite possible. They are extraordinarily rich in faces, and geometrically generally very well built. (fig. 13).

# Rhombic-bipyramidal.

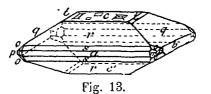
# a: b: c = 0.8494: 1: 0.8376.

Observed Forms.  $c = \{001\}$ , in most cases predominant and always well developed;  $q = \{011\}$ , with large faces;  $r = \{101\}$ , also large, but narrower than q;  $a = \{100\}$ , well developed and giving excellent images, just like  $b = \{010\}$ , whose faces are somewhat narrower;

5\*

 $s = \{201\}$  and  $t = \{012\}$ , well developed; there are commonly onlytwo faces of the form t present.

Further:  $o = \{121\}$ , showing among all pyramids present the largest faces;  $\omega = \{111\}$ , somewhat smaller than o;  $h = \{122\}$ , very small, but giving distinct images;  $m = \{110\}$  and  $p = \{120\}$ , very small and subsidiary, but measurable.



Dextrogyratory Triethylenediamine-Cobalti-rhodanide.

Angular V	alues :	Observ	ed:	Calcul	ated:
c : q = (001):	(011) =	*39°	57		
r : q = (101):		*56	56	-	_
r : s = (101):	(201) =	18	<b>23</b>	18°	31'
c : r = (001):	(101) =	44	39	44	36
s : a = (201):	(100) =	<b>26</b>	58	<b>26</b>	53
b: q = (010):	(011) =	50	<b>2</b>	50	3
s: q = (201):	(011) =	69	39	69	42
c : t = (001):	(012) ==	<b>22</b>	39	<b>22</b>	$43\frac{1}{2}$
t : q = (012):	(011) =	17	16	17	$13\frac{1}{2}$
$r: w = (\overline{1}0\overline{1}):$	(111) =	30	57	30	49
$w: o = (\overline{111}):$	$(\bar{1}2\bar{1}) =$	19	9	19	$12\frac{1}{2}$
$o : b = (\bar{1}2\bar{1}):$	(010) =	40	3	39	$58\frac{1}{2}$
c : h = (001):	: (122) =	44	4	44	11
$h : o = (1\overline{2}2)$ :	(121) =	73	0	73	$2\frac{1}{2}$
c : o = (001):	(121) =	62	51	<b>62</b>	46 <u>1</u>
o : o = (121)	: (121) ==	80	6	79	57
$p \circ : q = (\overline{121})$	:(011) =	81	56	81	$53\frac{1}{3}$
o : p = (121)	: (120) ==	<b>27</b>	9	<b>27</b>	9
a: m = (100):	(110) =	40	15	<b>4</b> 0	21
m: b = (110)	:(010) =	: 49	45	<b>4</b> 9	39
a : w = (100)	:(111) =	52	44	52	55
w:m=(111)	: (110) ==	: 37	<b>4</b> 6	37	42
w: c = (1, 1)	:(001) =	: 52	24	52	18

68

A distinct cleavage was not observed.

14

On {001}, {011} and {101} everywhere normal extinction. The crystals are not appreciably dichroitic. The optical axial plane is  $\{100\}$ ; the apparent axial angle is small, and the *c*-axis is first bisectrix.

The specific weight of the substance at 25°C was found to be :  $d_{A^{\circ}}^{25^{\circ}} = 1.502$ ; the molecular volume is: 275.26.

Topical parameters:  $\chi: \psi: \omega = 6.1893: 7.2867: 6.1034.$ 

With tepid water on {001} beautiful corrosion-figures were obtained after short treatment. They represented rectangular, pyramidal elevations, which were distinctly symmetrical with respect to the planes {100} and {010}. Consequently the crystals must be considered as having *bipyramidal* symmetry; with mixtures of alcohol and water rectangular, bilateral-symmetrical corrosion-figures were also obtained, which are in agreement with the holohedrical symmetry of the rhombic system.

XIII. Laevogyratory Luteo-Triethylenediamine-Cobalti-rhodanide.

#### Formula: {Co(Aein),}(CNS),

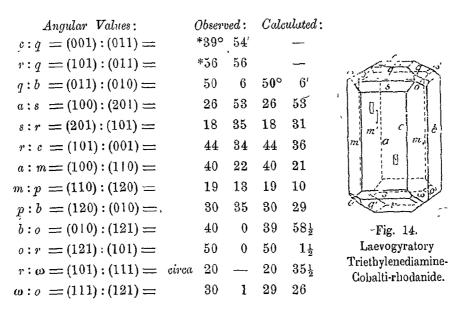
Thick, short-prismatic, orange- or blood-red needles, which are very well built, and which give excellent images. Although the habit is different from that of the dextrogyratory compound, the crystalform is evidently quite the same.

Rhombic-bipyramidal.

#### a:b:c = 0.8494:1:0.8375.

Observed Forms:  $b = \{010\}$ , predominant and, like  $a = \{100\}$ , which is also well developed, giving excellent images;  $c = \{001\}$ , small but very lustrous;  $s = \{201\}$  and  $r = \{101\}$ , rather large;  $q = \{011\}$ , somewhat larger yet, and like both foregoing forms, reflecting excellently;  $m = \{110\}$ , about as broad as r, and reflecting well;  $p = \{120\}$ , narrow and a little duller;  $o = \{121\}$ , well developed;  $\omega = \{111\}$ , with small faces between o and r. The habit is short-prismatic with respect to the *c*-axis, with predominance of 010} and {100}. (Fig. 14).

-



A distinct cleavage could not be found.

The optical properties are the same as indicated in the previous case.

The specific gravity of the crystals was pycnometrically determined to be:  $d \frac{25^{\circ}}{4^{\circ}} = 1.496$ ; the molecular volume is: 276.37.

Topical parameters  $\chi: \psi: \omega = 6.1979: 7.2968: 6.1110.$ 

Of a plate parallel to {001} we obtained a Röntgenogram which notwithstanding its imperfectness, in every case showed the presence of at least one plane of symmetry.

#### XIV. Racemic Luteo-Triethylenediamine-Cobalti-perchlorate.

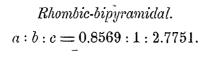
# Formula : $\{Co(Aein)_{s}\}(ClO_{4})_{s}$ .

The salt was prepared by double decomposition between the racemic bromide and silver-perchlorate.

It is rather difficult to obtain well developed crystals of this compound; commonly thin, rectangular, tabular crystals are obtained possessing round edges and giving considerably oscillating angular values; or they are complicated intergrowths of extremely thin plates ärranged in roseites. Between crossed nicols such intergrowths will in no situation show a complete extinction, but launellar polarisation and high interference-colours, in some cases also a mosaic-like structure:

Finally we succeeded in making the necessary measurements with the rectangular, tabular crystals.

70



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Fig. 15. Racemic Triethylenediamine-Cobaltiperchlorate.

Observed Forms:  $c = \{001\}$ , large and lustrous, in most cases striated parallel to the intersection: c:q;  $r = \{102\}$ ,  $o = \{111\}$  and  $q = \{011\}$ , about equally largely developed; commonly q gives the better, r the feebler images. Finally again:  $s = \{101\}$ , narrow, but easily measurable. The habit is tabular parallel to  $\{001\}$ , with a slight elongation parallel to the *b*-axis.

Angular	Values :	(	Observ	ed:	Calcul	ated:
c:q =	(001) : (011)	) == <sup>i</sup>	*70°	11'		-
c:r =	(001): (102	)=	* 58	20	· _	-
c : 0 ==	(001):(111	) ==	77	10	76°`	49'
c:s =	(001):(101	) =	72	56	72	50 <del>]</del>
s : s ==	(101): (101	) ==	<b>34</b>	8	<b>34</b>	$19\frac{1}{3}$
r:r =	(102): (102)	) ==	63	35	63	20
q:q =	(011):(01)	) =	40	$\overline{2}$	39	38
r:s =	(102) : (101)	),=	14	38	14	36

On  $\{001\}$  the extinction is perpendicular and parallel with respect to the intersections c:r and c:q. The plane of the optical axes is  $\{010\}$ ; the crystals are distinctly dichroitic, namely orange for vibrations parallel to the plane of the optical axes, orange-yellow for such as are perpendicular to it.

The specific weight of the crystals at 25°,1 C. was:  $d_{4_0} = 1.878$ ; the molecular volume is thus: 572.72.

Topical parameters:  $\chi : \psi : \omega = 5.3314 : 6.2217 : 17.2660.$ 

XV. Dextrogyratory Luteo-Triethylenediamine-Cobalti-perchlorate.

Formula :  $\{Co(Aein)_s\}(Cl O_4)_s$ .

The compound was prepared by transformation of the d-bromide by means of a solution of silver-perchlorate. The salt crystallizes from its aqueous solution in the shape of flat, brownish-red, very

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lustrous crystals, which show rather strong oscillations of their angular values, especially in the vertical zone. (Fig. 16).

They are rhombic bisphenoidic.

$$a:b:c=1.0572:1:0.6801.$$

Observed Forms:  $b = \{010\}$ , strongly predominant and rather sharply reflecting;  $a = \{100\}$ , very narrow or wholly absent, but with some crystals prominent;  $m = \{110\}$ , well developed, giving however multiple images;  $r = \{101\}$  and  $q = \{011\}$ , giving very sharp reflections;  $o = \{111\}$ , in most cases broader and larger than  $\omega = \{111\}$ ; this last form reflects very well.

Angular Values: Observed: Calculated:

 $b:q = (010):(011) = *55^{\circ} 47'$ b: o = (010): (111) = \*6014  $q:q = (011):(0\overline{1}1) = 68$  $\mathbf{26}$ 68° 26' o: r = (111): (101) = 2946  $\mathbf{29}$ 46 b: m = (010): (110) = 43 $\mathbf{28}$  $\mathbf{43}$  $24\frac{1}{2}$ m:a = (110): (100) = 463246 32î  $r:r = (101): (\overline{1}01) = 65$ 30 65 30 m:q = (110): (011) = 65**4**8 65 53 <del>,</del> q:r = (011):(101) = 464 45 56r: m = (101): (110) = 6816 68 10님 a: o = (100): (111) = 62- 3 61  $59\frac{1}{2}$ o: c = (111): (001) = 430 43 61  $b: \omega = (010)^{:}(1\overline{1}1) = 60$ 16 60 14  $\omega: r = (1\overline{1}1): (101) = 29$ 50 29 46

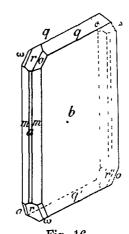


Fig. 16. Dextrogyratory Triethylenediamine-Cobalti-perchlorate.

No distinct cleavage was observed.

The specific gravity of the crystals was pycnometrically determined at 25° C., and found to be  $d \frac{25^{\circ}}{4^{\circ}} = 1.881$ , the molecular volume is thus: 285.80, and the topical axes are:  $\chi : \psi : \omega = 7.7731 : 7.3526$ ': 5.004.

# XVI. Laevogyratory Triethylenediamine-Cobalti-perchlorate.

# Formula: $\{Co(Aein)_{s}\}(ClO_{4})_{s}$ .

This salt was prepared from the corresponding *l*-bromide by means of silver-perchlorate, and the concentrated solution afterwards slowly evaporated at  $15^{\circ}$  C.

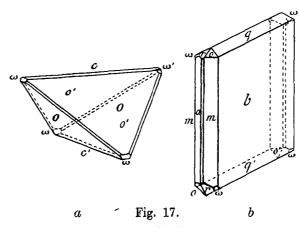
From an aqueous solution, still containing a trace of the silversalt in excess, the salt crystallized in the form of beautiful, sphenoidic crystals (fig. 17*a*), which immediately showed the presence of hemihedrical symmetry. From the pure solutions in most cases the flat, rectangular crystals, reproduced in fig. 17*b* were obtained; they had a brownish-red or brownish-yellow colour, and show more constant angular values than the sphenoidic crystals, whose angles oscillate and which possess considerable geometrical anomalies.

Evidently these kinds of crystals are however quite identical.

## Rhombic-bisphenoidic.

#### a:b:c = 1.0580:1:0.6806.

Observed Forms:  $b = \{010\}$ , highly predominant, and reflecting well; the faces are however often spoiled, and then give multiple reflections. Further  $m = \{110\}$ , giving good images and about as



Laevogyratory Triethylenediamine-Cobaltiperchlorate.

large as  $c = \{011\}$ , which form shows very lustrous faces;  $r = \{101\}$ , giving sharp images, and very well developed, about as large as  $o = \{111\}$ ;  $\omega = \{1\overline{1}1\}$  on the contrary small, and rather dull, although giving well defined images;  $a = \{100\}$ , very narrow and dull. In

the crystals drawn in fig. 17*a*, the form  $o = \{111\}$  is predominant;  $\omega = \{1\overline{1}1\}$  small and narrow,  $b = \{010\}$ , narrow but reflecting well, like  $a = \{100\}$ , which form is developed about équally to it;  $c = \{001\}$ in most cases absent, but rarely present with only one single curved and rudimentary face.

Angular Values:	Observ	ed:	Calcul	ated:
b : o = (010) : (111) =	*60°	12'		
b: m = (010): (110) =	*43	23		
b : q = (010) : (011) =	55	48	55°	46'
a : m = (100) : (110) =	46	39	46	37
$q : q = (011) : (0\overline{1}1) =$	68	28	68	$28\frac{1}{2}$ -
$\omega: b = (1\overline{1}1): (0\overline{1}0) =$	60	13	60	$12\frac{2}{3}$
$\omega: r = (1\overline{1}1): (101) =$	<b>29</b>	49	<b>29</b>	45
$r : a = (101) : (\overline{1}00) =$	57	12	57	17
r : r = (101) : (101) =	65	43	65	36
a : o = (100) : (111) =	62	0	62	0
c : o = (001) : (111) =	<b>43</b>	0	43	8
$o: \omega = (111): (11\overline{1}) =$	93	48	93	44
$\omega: o = (\overline{1}11): (111) =$	55	11	55	46
$o : \omega = (111) : (111) =$	59	50	59	32
$o : o = (111) : (1\overline{11}) =$	86	13	86	16

No distinct cleavage could be observed.

Feebly dichroitic: on  $\{010\}$  for vibrations parallel to the *a*-axis orange-yellow; for those perpendicular to these, yellow-orange.

The plane of the optical axis is  $\{001\}$ ; the *a*-axis is probably first bisectrix.

The specific gravity of the crystals was pycnometrically determined to be:  $d \frac{25^{\circ}}{4^{\circ}} = 1.888$ ; the molecular volume is thus: 284.74.

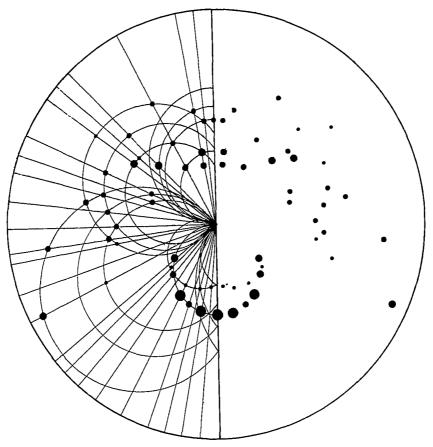
Topical parameters.  $\chi:\psi:\omega=7.7657:7.3399:4.9955.$ 

XVII. Racemic Triethylenediamine-Cobalti-nitrite.

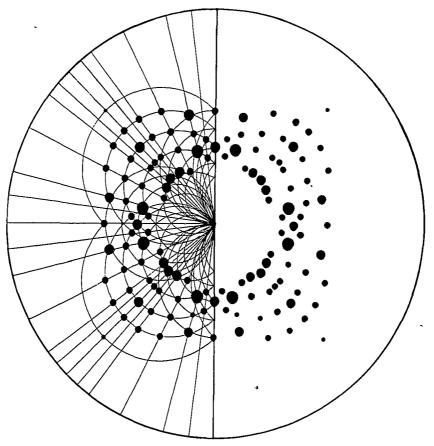
Formula:  $\{Co(Aein)_{s}\}(NO_{2})_{s}$ 

Thin, orange-yellow, in thicker layers orange-brown, hexagonal plates, often showing mutilated faces, and intergrowths parallel  $\{0001\}$ ;  $m: m : = (1010) : (0110) = 60^{\circ}$ ;  $m: c = 1010) : (0001) = 90^{\circ}$ .

Prof. Dr. F. M. JAEGER, "Investigations on Pasteur's Principle of the Relation between Molecular and Physical Dissymmetry." II.



A. Stereographical Projection of the Röntgenogram of the pseudo-ditrigonal racemic [Co (Aein)<sub>3</sub>]  $Br_3 + 3H_2O$ ; plate perpendicular to the *c*-axis.



B. Stereographical Projection of the Röntgenogram of dextrogyratory- and laevogyratory [Co Aein)<sub>3</sub>] + 2 H O; plate perpendicular to the *c*-axis.

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