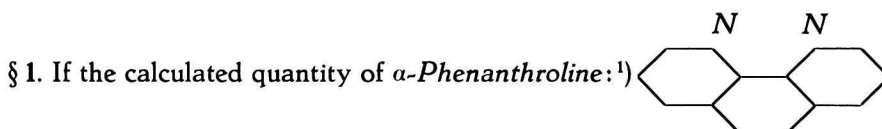
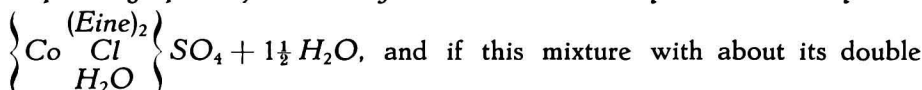


**Chemistry.** — “On racemic and optically-active *α*-Phenanthroline-diethylenediamine-Cobaltic-Salts and on the Reaction between Mono- or Diamines and Diethylenediamine-dichloro- or -chloro-aquo-Salts.” By Prof. F. M. JAEGER.

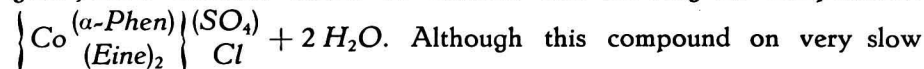
(Communicated at the meeting of February 27, 1926).



mpt.: 173° C., prepared after BLAU's method<sup>2)</sup>, be added to the corresponding quantity of *Diethylenediamine-chloro-aquo-Cobaltic-sulphate*:



weight of water be heated during 6 or 8 hours with a small flame in a flask with hemi-spherical bottom and provided with a reflux-cooler, — the original lilac-red colour of the solution gradually changes into a yellowish-brown one. After cooling during 24 hours, small brownish-yellow, thin, tabular crystals are deposited, while by careful evaporation of the mother-liquor again a fresh quantity of the same salt may be obtained. Finally a viscous liquid remains, from which a small quantity of small, dark-brown crystals are deposited, but which does not completely crystallize, even after a long time. The first deposited, brownish-yellow product appears to be a *Chlorosulphate* of an *α*-Phenanthroline-diethylenediamine-Cobaltic ion. The salt can be purified by recrystallisation; it is finally obtained in the shape of beautiful, very brittle, gold-yellow needles, united in clusters, and showing the composition:



Although this compound on very slow evaporation of its solutions can be obtained in thicker needles, it is, however, not possible to study them accurately, because they have strongly varying angular values and, moreover, do not possess sufficiently developed terminal facets. The needles are triclinic, have oblique and mostly un-

<sup>1)</sup> The base is also called: *Pseudo-phenanthroline* and crystallizes with 4 H<sub>2</sub>O, which it loses, however, by heating at 100° C.

<sup>2)</sup> F. BLAU; Monatshefte, 19, 647, (1898).

dulatory extinction and are only feebly dichroitic. In one of the terminal zones angles of  $83^{\circ}25'$ ,  $33^{\circ}16'$  and  $63^{\circ}12'$  were measured; in the vertical zone such of  $86^{\circ}$  or  $87^{\circ}$ , and of  $16^{\circ}$ ,  $24^{\circ}$  and  $63^{\circ}$ . The complex ion is precipitated by a solution of *NaI* in the form of an orange coloured *iodide*, which is sparsely soluble in water, and which by slow evaporation of its only very weakly concentrated solution, can be obtained in the form of small, dark brown crystals. They are anhydrous and have the composition:  $\left\{ \text{Co} \begin{matrix} (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{matrix} \right\} \text{I}_3$ ; their full description is given further on.

The dark brown crystals, however, which were obtained from the mother-liquor, were proved to be for the greater part such of *Triethylenediamine-Cobaltic-chlorosulphate*, with its characteristic *ditrigonal-scalenohedral* crystalform: finally the viscous mother-liquor gives by precipitation with *NaI*, moreover, an *iodide*, which could be obtained, on slow evaporation, in measurable crystals, which appeared to be identical with those of *racemic Triethylenediamine-Cobaltic-iodide*.

From this it is evident, that the complex *Diethylenediamine-chloro-aquo-Cobaltic-ion* is partially decomposed during the reaction, with simultaneous formation of the apparently highly stable *Triethylenediamine-ion*; partially, however, the reaction has occurred in the normal way, i.e. by substitution of the  $\text{H}_2\text{O}$ -group and the *Cl*-atom of the complex-ion by one molecule of  *$\alpha$ -Phenanthroline*.

*Analysis of  $\alpha$ -Phenanthroline-diethylenediamine-Cobaltic-chlorosulphate*: 0,2820 gramme of the substance gave 0,1246 gramme  $\text{BaSO}_4$  and 0,0794 gramme  $\text{AgCl}$ . Therefore: 6,96% *Cl* and 18,2% ( $\text{SO}_4$ ). The determination of the water-content gave: 6,81%  $\text{H}_2\text{O}$ .

Calculated for  $\left\{ \text{Co} \begin{matrix} (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{matrix} \right\} \text{Cl} + 2 \text{H}_2\text{O}$ : 6,83%  $\text{H}_2\text{O}$ : 6,74% *Cl* and 18,23% ( $\text{SO}_4$ ).

The *Iodide* gave in the same way: 51,3% *I*; calculated for  $\left\{ \text{Co} \begin{matrix} (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{matrix} \right\} \text{I}_3$ : 51,49% *I*.

The compound was anhydrous and only very sparsely soluble in water.

The last mother-liquor but one gave dark brown crystals of *rhombic-bipyramidal* symmetry; forms observed:  $c = \{001\}$ , predominant;  $s = \{021\}$  and  $q = \{041\}$ , the last form much broader than  $s$ ;  $o = \{111\}$ , well developed;  $\omega = \{221\}$ , narrow;  $\delta = \{113\}$ , extremely narrow. The following measurements were made:  $c : o = 53^{\circ}10'$ ;  $c : q = 73^{\circ}39'$ ;  $c : s = 60^{\circ}$ ;  $o : o' = 74^{\circ}50'$ ;  $o : o_4 = 62^{\circ}27'$ ;  $o : q = 48^{\circ}18'$ . The habitus of the crystals is elongated parallel to the *a*-axis, with flattening parallel  $\{001\}$ . Later also small octahedral-shaped crystals were obtained, which showed only  $o = \{111\}$  and, very small,  $c = \{001\}$ . From the last mother-liquor thick, kite-shaped crystals were obtained, which showed  $c = \{001\}$  very well developed, and furthermore:  $o = \{111\}$ , large and lustrous and  $\omega = \{221\}$ , very narrow. Measurements:  $c : o = 53^{\circ}8'$ ;  $o : o' = 74^{\circ}48'$ ;  $o : \omega = 16^{\circ}3'$ ;  $o : q = 48^{\circ}15'$ . From these data it becomes evident that no other substance than *racemic  $\{ \text{Co} (\text{Eine})_3 \} \text{I}_3 + 1 \text{H}_2\text{O}$*  is present here,

as described formerly<sup>1)</sup>; in the measurements given formerly, the *c*-axis was taken with double the value adopted here.

Analysis : 59,9 0/0 I; calculated: 59,7 0/0.

§ 2. Crystalform of racemic  $\left\{ \begin{array}{l} \text{Co} \text{ (} \alpha\text{-Phen) } \\ \text{(Eine)}_2 \end{array} \right\} I_3$ .

From water the salt is deposited in very small, brown crystals, which can accurately be measured (Fig. 1).

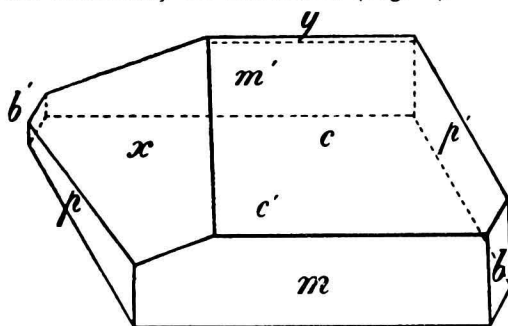


Fig. 1.

*Triclinic-pedial.*

$a : b : c = 0,6487 : 1 : 0,4692$ ;  
 $A = 100^\circ 2\frac{1}{2}'$ ;  $a = 111^\circ 13\frac{1}{2}'$ .  
 $B = 121 9$  ;  $\beta = 125 53$ .  
 $C = 75 53$  ;  $\gamma = 66 39$ .

Forms observed:  $c = \{001\}$ , lustrous, well developed, but smaller than  $c' = \{00\bar{1}\}$ , which form appears striated parallel to the edge  $c' : p'$ ;  $m = \{110\}$  and  $p = \{1\bar{1}0\}$ , well developed

and lustrous;  $m' = \{\bar{1}\bar{1}0\}$ , is duller than  $m$ , and the same holds, in somewhat smaller degree, for  $p' = \{\bar{1}\bar{1}0\}$ ;  $b = \{010\}$  and  $b' = \{0\bar{1}0\}$ , very lustrous, but much narrower than  $m$  and  $p$ ;  $y = \{\bar{1}\bar{1}1\}$ , narrow but yielding good reflections;  $x = \{1\bar{4}9\}$ , large and lustrous, but making rather varying angles with  $p$ ,  $m$  and also with  $c$ . The habitus is tabular parallel to  $c'$ , with a slight elongation parallel to the edge  $c : m$ . No distinct cleavage was observed.

<i>Angular values :</i>	<i>Observed :</i>	<i>Calculated :</i>	
$m : p = (110) : (\bar{1}\bar{1}0) =$	*58°	3'	—
$p : b' = (\bar{1}\bar{1}0) : (0\bar{1}0) =$	*50	12½'	—
$m : c = (110) : (001) =$	*52	56	—
$p : c = (\bar{1}\bar{1}0) : (001) =$	*70	37	—
$c : y = (001) : (\bar{1}\bar{1}1) =$	*47	31	—
$b : m = (010) : (110) =$	71	44½'	71° 44½'
$c : x = (001) : (1\bar{4}9) = ca.$	12	30	12 20
$m : x = (110) : (1\bar{4}9) =$	53	55	53 34
$m' : y = (\bar{1}\bar{1}0) : (\bar{1}\bar{1}1) =$	79	33	79 33

On all faces oblique extinction. Strongly dichroitic: on  $x$  for vibrations almost parallel to the  $a$ -axis: orange, for such perpendicular to it: blood-red.

From these measurements it is clear that this *iodide* shows no form-analogy with that of the *Triethylenediamine-Cobaltic-ion*.

For a fuller description of the properties of the new complex-ion, also

<sup>1)</sup> F. M. JAEGER. Rec. des Trav. Chim. d. Pays-Bas, 38, 205, 206. (1919).

a number of some other salts were prepared by reaction of the *iodide* with different *silver-salts*. Besides the *chlorosulphate* and *iodide* already mentioned above, also the following salts were obtained in a well crystallized form: the *sulphate*, the *nitrate* and the *chlorate*, which salts crystallize respectively with 12, 0, and 1 molecules of water. Their crystalform is described below. Also the corresponding *bromide* was prepared by double decomposition with *AgBr* and evaporation of the solution. The crystallized salt is anhydrous, or contains perhaps 0,5 molecule  $H_2O$ . On slow evaporation of the solution only very thin needles are obtained, which are only rudimentarily developed and unsuitable for measurement.

§ 3. Crystalform of racemic  $\left\{ \begin{array}{l} (a-Phen) \\ (Eine)_2 \end{array} \right\} Co (NO_3)_3$ .

Beautiful, small, highly lustrous crystals were obtained from an aqueous solution, containing some *silvernitate* in excess. (Fig. 2).

*Triclinic-pedial.*

$$a : b : c = 0,9938 : 1 : 0,8574;$$

$$A = 91^\circ 0' ; a = 88^\circ 22'.$$

$$B = 104 13 ; \beta = 104 16\frac{2}{3}.$$

$$C = 100 33 ; \gamma = 100 40.$$

*Forms observed:*

$a = \{100\}$ , predominant, yielding very sharp images, sometimes striated diagonally;  $a' = \{\bar{1}00\}$ , also large and lustrous;  $b' = \{010\}$ , well developed and highly lustrous;  $b = \{0\bar{1}0\}$ , narrow;  $c = \{001\}$ ,

broader than  $b$ ;  $c' = \{00\bar{1}\}$ , narrower than  $c$ , but well reflecting;  $r = \{\bar{1}01\}$ , very sharply reflecting, narrower than  $c$  and than  $s = \{10\bar{1}\}$ , which form yields extremely good reflections;  $m = \{110\}$ , large, occasionally vertically striated;  $p' = \{\bar{1}10\}$ , narrow, but well measurable;  $n' = \{\bar{1}10\}$ , narrower than  $m$ , not striated and very lustrous;  $q' = \{01\bar{1}\}$ , eminently reflecting;  $q = \{0\bar{1}1\}$ , smaller than  $q'$ , yielding good images;  $t = \{30\bar{2}\}$ , very narrow, but well measurable. The habitus of the crystals is thick tabular parallel  $\{100\}$ , sometimes prismatic parallel to the  $c$ -axis, but occasionally elongated in the direction of the  $b$ -axis.

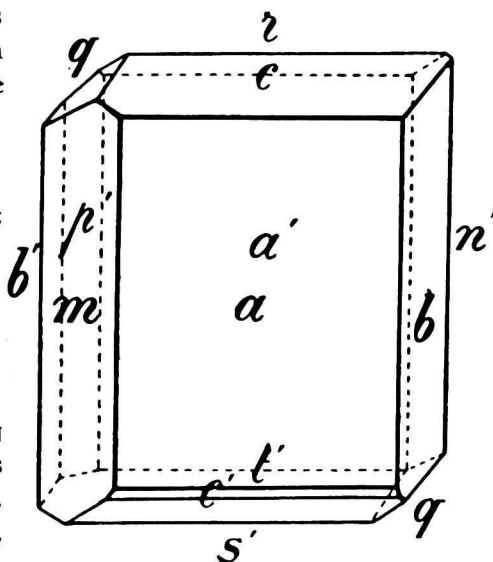


Fig. 2.

*Angular values:*

*Observed: Calculated:*

$a : b = (100) : (010) =$	$*79^\circ 27'$	—
$a : c = (100) : (001) =$	$*75 47$	—
$b : c = (010) : (001) =$	$*89 0$	—

<i>Angular values :</i>	<i>Observed :</i>	<i>Calculated :</i>
$a : m = (100) : (\bar{1}\bar{1}0) = *48$	27	—
$c : r = (001) : (\bar{1}01) = *47$	19	—
$b : n' = (010) : (\bar{1}\bar{1}0) = 51$	46	$51^\circ 21\frac{1}{3}'$
$a' : p' = (\bar{1}00) : (\bar{1}\bar{1}0) = 38$	38	38 49
$p' : b' = (\bar{1}\bar{1}0) : (0\bar{1}0) = 40$	49	40 38
$a' : r = (\bar{1}00) : (\bar{1}01) = 56$	54	56 54
$n' : q' = (\bar{1}\bar{1}0) : (01\bar{1}) = 57$	2	56 58
$q' : s' = (01\bar{1}) : (10\bar{1}) = 53$	1	53 $10\frac{1}{2}$
$s : m = (10\bar{1}) : (\bar{1}\bar{1}0) = 69$	57	69 $51\frac{1}{2}$
$c : m = (001) : (\bar{1}\bar{1}0) = 79$	24	79 30
$b : q' = (010) : (01\bar{1}) = 50$	22	50 22
$q' : c = (01\bar{1}) : (00\bar{1}) = 40$	38	40 38
$a : q = (100) : (0\bar{1}\bar{1}) = 84$	32	84 23
$c' : s' = (00\bar{1}) : (10\bar{1}) = 47$	20	47 19
$c' : t' = (00\bar{1}) : (30\bar{2}) = 65$	28	65 36
$a : t' = (30\bar{2}) : (100) = 38$	45	38 37

No distinct cleavability was observed.

On  $\{100\}$  the direction of the plane of the optical axes includes  $24^\circ$  with the  $c$ -axis; one of the branches of the hyperbola can be seen at the border of the field of the microscope. Strongly dichroitic: orange and yellow.

§ 4. *Crystalform of racemic*  $\left\{ \begin{array}{l} \text{Co}^{(\alpha\text{-Phen})} \\ \text{(Eine)}_2 \end{array} \right\}_2 (\text{SO}_4)_3 + 12 \text{H}_2\text{O}$ .

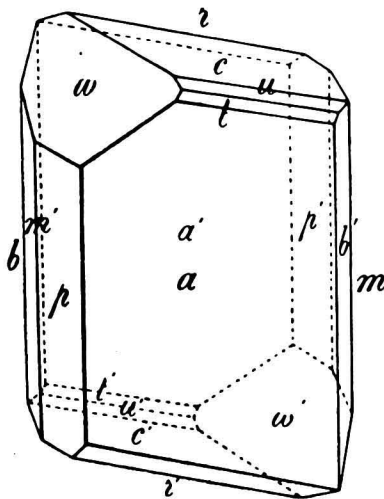


Fig. 3.

This compound crystallizes from its aqueous solution in flat, pale brown and very lustrous crystals, which have quadratic or hexagonal limits. (Fig. 3).

*Triclinic-pinacoidal.*

$$a : b : c = 1,4062 : 1 : 0,7362;$$

$$A = 101^\circ 15'; \alpha = 93^\circ 19'.$$

$$B = 51 \ 33; \beta = 52 \ 51.$$

$$C = 75 \ 56; \gamma = 80 \ 53.$$

*Forms observed:*  $a = \{100\}$ , large and lustrous;  $b = \{010\}$ , narrower than  $c = \{001\}$ , both yielding very sharp images;  $m = \{110\}$

and  $p = \{1\bar{1}0\}$ , also very lustrous,  $p$  ordinarily narrower than  $m$ ;  $r = \{\bar{2}01\}$ , well developed, yielding good reflections, mostly with only one face present;  $s = \{\bar{3}01\}$ , narrow, but well measurable;  $\omega = \{1\bar{1}1\}$ , large and well reflecting; sometimes also:  $t = \{201\}$ , very narrow, just as:  $u = \{101\}$ . The habitus is tabular parallel to  $\{100\}$ , and almost equally developed in the directions of  $b$ - and  $c$ -axis.

<i>Angular values :</i>	<i>Observed :</i>		<i>Calculated :</i>	
$a : c = (100) : (001) =$	*128°	27'	—	—
$a : b' = (100) : (0\bar{1}0) =$	*75	56	—	—
$c : b' = (001) : (0\bar{1}0) =$	*101	15	—	—
$b' : p = (0\bar{1}0) : (1\bar{1}0) =$	*35	23	—	—
$b' : \omega = (0\bar{1}0) : (1\bar{1}1) =$	*56	6	—	—
$a : \omega = (100) : (1\bar{1}1) =$	86	47½	86°	51½
$\omega : p = (1\bar{1}1) : (1\bar{1}0) =$	66	2	66	1½
$\omega : c = (1\bar{1}1) : (001) =$	54	6	54	7
$c : p = (001) : (1\bar{1}0) =$	59	52	59	51½
$c : r = (001) : (\bar{2}01) =$	26	23	26	34½
$a' : r = (\bar{1}00) : (\bar{2}01) =$	25	10	24	58½
$c : s = (001) : (\bar{3}01) =$	32	5	32	2
$s : a' = (\bar{3}01) : (\bar{1}00) =$	19	28	19	31
$m : c = (110) : (001) =$	72	5	72	5
$a : p = (100) : (1\bar{1}0) =$	40	36	40	33
$m : b = (110) : (010) =$	47	35	47	47½
$m : a = (110) : (100) =$	56	29	56	16½
$m : \omega = (1\bar{1}0) : (1\bar{1}1) =$	63	47	63	25
$a : t = (100) : (201) =$	60	5	60	0
$t : u = (201) : (101) =$	36	43	36	39
$u : c = (101) : (001) =$	31	39	31	48

A distinct cleavage was not found.

The direction of the plane of the optical axes on  $\{100\}$  is almost parallel to the  $c$ -axis. On  $\{100\}$  one of the branches of the hyperbola is visible in convergent polarized light. No appreciable dichroism is present.

The water-content was found to be: 17,5 %; calculated: 17,6 %  $H_2O$ .

§ 5. *Crystalform of racemic*  $\left. \begin{array}{l} Co \\ (Eine)_2 \end{array} \right\} (ClO_3)_3 + 1H_2O$ .

From an aqueous solution this salt is deposited in the form of dark

brown thin prisms, which show a great number of faces. (Fig. 4).

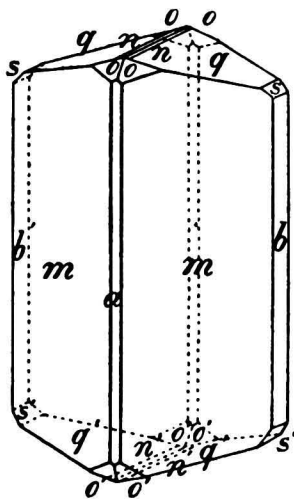


Fig. 4.

*Rhombic-bipyramidal.*

$$a : b : c = 0,6538 : 1 : 0,2936.$$

*Forms observed:*  $m = \{110\}$ , large and lustrous;  $q = \{011\}$ , well developed and giving sharp reflections;  $o = \{211\}$ , smaller than  $q$ , often dull;  $b = \{010\}$ , very narrow, but yielding sharp images;  $a = \{100\}$ , mostly absent, sometimes present with only a single face and dull;  $s = \{031\}$ , small, but giving clear, somewhat faint images;  $n = \{012\}$  and  $p = \{150\}$ , scarcely visible, yielding only very faint reflections. The habit is elongated in the direction of the  $c$ -axis.

*Angular values:*

*Observed: Calculated:*

$m : b = (110) : (010) =^*$	56°	49½'	—
$m : q = (110) : (011) =^*$	81	8	—
$b : q = (010) : (011) =$	73	28	73° 38½'
$q : q = (011) : (0\bar{1}1) =$	33	6	32 43½'
$b : s = (010) : (031) =$	48	33	48 38
$s : q = (031) : (011) =$	25	9	25 5½'
$q : n = (011) : (012) =$	8	7	8 0½'
$n : n = (012) : (0\bar{1}2) =$	16	50	16 42
$m : o = (110) : (211) =$	48	37	48 27
$o : q = (211) : (0\bar{1}1) =$	50	15	50 25
$a : m = (100) : (110) =$	33	10½'	33 10½'
$b : p = (010) : (150) =$	17	7	17 0½'
$p : m = (150) : (110) =$	39	42	39 49½'
$o : q = (211) : (011) =$	40	50	40 45½'
$m : o = (110) : (2\bar{1}1) =$	64	36	64 33

Cleavable parallel to  $q$ .

On  $m$  normally orientated extinction. No axial image was observed. The water-content was determined as: 3 %; calculated: 2,89 %  $H_2O$ .

§ 6. It is characteristic that the replacement of one molecule *ethylenediamine* in the complex *Triethylenediamine-Cobaltic-ion* by one molecule of another bivalent base appears in general to lower the degree of symmetry of the crystalforms of these compounds in an appreciable degree, as becomes evident by comparison of the crystalforms mentioned above with those of the corresponding *Triethylenediamine-Cobaltic-derivatives*. Indeed, by such a substitution the symmetry of the complex

ion, originally consisting in the presence of a ternary and three binary axes, is reduced to that characterized by the presence of a single binary axis<sup>1)</sup>. However, the new ion remains, as the original one, merely *axially-symmetrical*, and for this reason it will possibly exist in two non-superposable mirror-configurations.

It was tried to separate both these enantiomorphous forms of the compound: 1<sup>o</sup>. by means of the *d-tartrate*; 2<sup>o</sup>. by the aid of the *bromo-d-camphorsulphonate*. Both these compounds were prepared, starting from the *bromide*, by means of the calculated quantity of *silver-d-tartrate*, respectively *silver-d-bromo-camphorsulphonate*. The two salts thus obtained, crystallized very well. The *d-tartrate* shows in solutions only a slight rotation, which totally depends on the *d-tartaric acid*, which the salt contains; this is also evident from the fact, that the rotatory dispersion appeared to be only weak and of quite normal character. Also the *iodide* obtained from this *tartrate* by precipitation with *NaI*, was proved to be completely *inactive*. Evidently only the *a-tartrate* of the *racemic* ion is present here; its crystalform is described in the following.

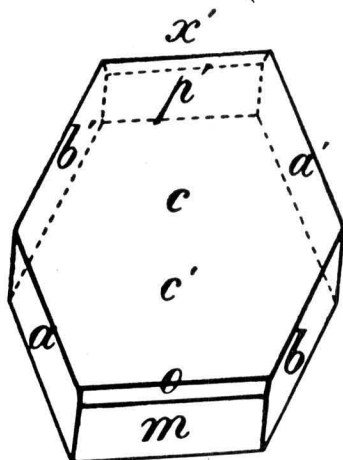
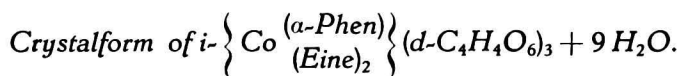


Fig. 5.

This salt crystallizes from water in thin hexagonal plates of a brownish-yellow colour. They are well built and show very lustrous facets (Fig. 5).

*Triclinic-pedial.*

$$\begin{aligned} a : b : c &= 1,1249 : 1 : 0,9207; \\ A &= 101^\circ 30\frac{1}{2}' ; a = 125^\circ 57'. \\ B &= 105 \ 58 \ ; \ \beta = 127 \ 25. \\ C &= 44 \ 30\frac{1}{2}' ; \ \gamma = 35 \ 23. \end{aligned}$$

*Forms observed:*  $c = \{001\}$  and  $c' = \{00\bar{1}\}$ , large and highly lustrous;  $a = \{100\}$ ,  $a' = \{\bar{1}00\}$ ,  $b = \{010\}$ , and  $b' = \{0\bar{1}0\}$ , all about equally well developed and giving excellent reflections;  $m = \{110\}$  and  $p' = \{\bar{1}10\}$ , well developed and lustrous;  $x = \{11\bar{1}\}$ , large and giving sharp images;  $x' = \{\bar{1}\bar{1}1\}$ , narrow and somewhat duller;  $o = \{111\}$ , very narrow and yielding faint images only. The habit of the crystals is thin tabular parallel to  $\{001\}$ , often with elongation parallel to the edge  $c : m$ .

<i>Angular values :</i>	<i>Observed :</i>	<i>Calculated :</i>
$a : b = (100) : (010) =$	$*135^\circ 29\frac{1}{2}'$	—
$b : c = (010) : (001) =$	$*78 \ 29\frac{1}{2}$	—
$a : c = (100) : (001) =$	$*74 \ 2$	—

<sup>1)</sup> This axis is polar and connects the centre of the  $\alpha$ -Phenanthroline-molecule with the middle of the opposite edge of the octahedron.



<i>Angular values :</i>	<i>Observed :</i>	<i>Calculated :</i>		
$a : m = (100) : (110) =$	*77	13	—	
$c' : x = (00\bar{1}) : (11\bar{1}) =$	*58	13	—	
$a : x = (100) : (11\bar{1}) =$	95	5	95°	1 $\frac{2}{3}$ '
$b : x = (010) : (11\bar{1}) =$	70	33	70	49
$b : m = (010) : (110) =$	58	16 $\frac{1}{2}$	58	16 $\frac{1}{2}$
$c : o = (001) : (111) =$	25	5	24	48
$o : m = (111) : (110) =$	27	21	27	31
$c : m = (001) : (110) =$	52	26	52	19
$m : x = (110) : (11\bar{1}) =$	69	21	69	28

No distinct cleavage was observed.

The direction of the optical axial plane on {001} includes an angle of 6° with the edge  $c : o$ . The crystals are only unappreciably dichroitic.

The water-content was: 11,9 %; calculated: 11,8 %  $H_2O$ .

§ 7. On the other hand the *d-bromocamphorsulphonate* mentioned before appeared to manifest only a weak rotation of its solution for *Na*-light; but this proved to be appreciably greater for smaller wave-lengths, while also the rotatory dispersion appeared to be distinctly abnormal, with a COTTON-effect in the vicinity of an absorption-band in the blue-violet part of the spectrum. Later it was proved, moreover, that the *iodide* prepared from this *d-bromocamphorsulphonate* by means of *NaI*, was indeed appreciably active in solution; more particularly, it was proved to be the salt of the *levogyrotory* ion. Tentatives to execute the fission into optical antipodes by means of *sodium- $\alpha$ -camphornitronate* gave hitherto no positive results.

Crystalform of  $l\left\{ \begin{array}{l} Co \\ (Eine)_2 \end{array} \right\} \begin{array}{l} (\alpha-Phen) \\ (d-Bromocamphorsulfon)_3 \end{array} + 3 H_2O$ .

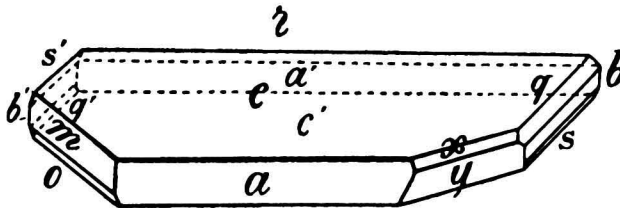


Fig. 6.

Very thin, orange or yellow, often badly built crystalplates (Fig. 6).

*Triclinic-pedial.*

$$\begin{aligned}
 a : b : c &= 1,2356 : 1 : 2,1156. \\
 A &= 82^\circ 8' ; a = 82^\circ 22'. \\
 B &= 103 38 ; \beta = 103 30\frac{1}{2}. \\
 C &= 88 9 ; \gamma = 89 58.
 \end{aligned}$$

*Forms observed:*  $c = \{001\}$  and  $c' = \{00\bar{1}\}$ , both predominant and yielding very sharp reflections;  $a = \{100\}$  and  $a' = \{\bar{1}00\}$ , well developed and very lustrous;  $b = \{010\}$ , narrow, well measurable;  $q = \{011\}$ , narrow, giving only faint images;  $s = \{01\bar{1}\}$ , broader and well reflecting; the corresponding forms:  $b' = \{010\}$ ,  $q' = \{0\bar{1}1\}$  and  $s' = \{0\bar{1}\bar{1}\}$  are mostly absent or are scarcely visible;  $r = \{\bar{1}01\}$ , well developed and yielding sharp reflexes;  $m = \{\bar{1}10\}$ , rather broad, dull;  $o = \{\bar{1}\bar{1}\bar{1}\}$ , narrower than  $m$ , but reflecting a little better;  $x = \{221\}$ , narrow, but well measurable;  $y = \{11\bar{1}\}$ , broader than  $x$  and excellently reflecting. The habitus is thin tabular parallel to  $\{001\}$ , with an elongation in the direction of the  $b$ -axis. The angles vary commonly within rather wide limits.

<i>Angular values :</i>	<i>Observed :</i>	<i>Calculated :</i>	
$c : a = (001) : (100) =$	$*76^{\circ} 22'$	—	
$c : b = (001) : (010) =$	$*97$	—	
$c : r = (001) : (\bar{1}01) =$	$*70$	—	
$q : c = (011) : (001) =$	$*70$	—	
$c : s = (001) : (01\bar{1}) =$	$*57$	—	
$a : q = (100) : (011) =$	$85$	$56$	$86^{\circ} 26'$
$b : q = (010) : (011) =$	$26$	$58$	$27$ $19$
$b : s = (010) : (01\bar{1}) =$	$24$	$22$	$24$ $18$
$c : x = (001) : (221) =$	$76$	$58$	$77$ $14$
$x : y = (221) : (11\bar{1}) =$	$31$	$29$	$31$ $8\frac{1}{2}$
$c' : y = (00\bar{1}) : (11\bar{1}) =$	$71$	$27$	$71$ $37$
$c : m = (001) : (1\bar{1}0) =$	$75$	$26$	$75$ $28$
$m : o = (1\bar{1}0) : (1\bar{1}\bar{1}) =$	$21$	$2$	$21$ $51$
$c' : o = (00\bar{1}) : (1\bar{1}\bar{1}) =$	$83$	$0$	$82$ $41$
$a : y = (100) : (11\bar{1}) =$	$60$	$3$	$60$ $30$
$y : s = (11\bar{1}) : (01\bar{1}) =$	$36$	$37$	$36$ $47$
$a' : s = (\bar{1}00) : (01\bar{1}) =$	$82$	$21$	$82$ $43$
$a : m = (100) : (1\bar{1}0) =$	$39$	$43$	$39$ $50$
$a : o = (100) : (1\bar{1}\bar{1}) =$	$42$	$55$	$42$ $49$
$a : x = (100) : (221) =$	$50$	$5$	$50$ $37$

No distinct cleavage was stated.

On  $\{001\}$  the extinction is practically parallel, respectively perpendicular to the edge  $c : r$ ; the plane of the optical axes is parallel to  $\{010\}$ . Only slightly dichroitic: orange and orange-yellow.

The determination of the water-content gave:  $3.87\%$   $H_2O$ ; calculated:  $3.93\%$  for  $3 H_2O$ .

§ 8. The possibility of a fission of the complex ion by means of the *d*-bromocamphorsulphonates thus being demonstrated, the fission considered

was started now in a systematical way and trials were made to isolate the pure dextro- and levogyrotory components by the aid of fractional crystallisation.

We started always with the racemic *bromide*, prepared from the solution of the corresponding *iodide* by treating this with freshly precipitated and washed *silverbromide*; the *bromide* thus obtained was several times recrystallized from water. By adding pure *silver-d-bromocamphorsulphonate* ( $+ 1\frac{1}{2} H_2O$ ) in the calculated quantity to its solution and by heating it on the waterbath, after filtration a clear orange-yellow solution is obtained, which after evaporation on the waterbath and after cooling yields a pale, salmon-coloured salt as principal product, crystallizing in small, lustrous tables. The mother-liquor deposits, after being kept for some time at roomtemperature, pale yellow flat needles or small tables; in this way in total six fractions were separated, until finally the last mother-liquor solidifies into a soft, almost resinous, pale orange-coloured mass, in which again some spare small crystals are included, which were eliminated from it by means of a pincet.

The first fraction appeared to be the *d-bromocamphorsulphonate* of the *levogyrotory* ion, already mentioned before; the last fraction, after conversion into the *iodide*, appeared to yield a mixture, consisting principally of the corresponding derivative of the *dextrogyrotary* ion, accompanied by a small quantity of the racemic *iodide*. The second fraction was the same as the first, its rotatory power being, however, somewhat lessened by the admixture of a little quantity of the salt of the dextrogyrotory component; the third and fourth fractions were only feebly levogyrotory and gave, after conversion into the *iodide*, chiefly the optically inactive salt. The fifth fraction was strongly dextrogyrotory; after conversion into the *iodide* this appeared also to be dextrogyrotory, but with admixture of an appreciable quantity of the racemic salt. From these data it becomes obvious that the fission by means of the *d-bromocamphorsulphonic acid* goes on in such a way, that first the less soluble *d-bromocamphorsulphonic* of the *levogyrotory* ion is deposited: the corresponding salt of the dextrogyrotory ion is far more soluble and is found accumulated principally in the last mother-liquids, which crystallize with difficulty. Both the optically-active *iodide*, separated from the *d-bromocamphorsulphonates* by means of *NaI*, appeared to be far more soluble than the racemic *iodide*: a fact making it possible to free the active *iodides* for the greater part from admixed racemic *iodide*. The greater solubility of the optically-active salts in comparison with that of the racemic compounds is in full agreement with the fact, that under ordinary circumstances the antipodes are really metastable with respect to the racemic compound. It is remarkable, that the racemic *iodide* possesses a somewhat deeper, more orange- or reddish-tinged colour than the more pale orange-coloured optically-active *iodides*; the same holds for their solutions. The rotations and rotatory dispersions

Observed, specific and molecular Rotations of the Solutions of anhydrous $l-\left\{ \text{Co} \begin{matrix} (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{matrix} \right\}-(d\text{-bromocamphorsulphon.})_3$			
The solution contained 0,4136 gramme of salt, i. e. 0,3975 gramme of the anhydrous substance in 100 ccm. solution. Length of the tube: 1 dm.			
Wave-length $\lambda$ in A. U.:	Rotation $\alpha$ observed:	Specific Rotation $[\alpha]$ :	Molecular Rotation $[M]$ :
6850 tot 6258	+ 0.17 <sup>o</sup> -	+ 42.8 <sup>o</sup>	+ 564.1
6090	+ 0.13 <sup>-</sup>	+ 32.7	+ 431.4
5940	+ 0.07 <sup>+</sup>	+ 17.7	+ 234.1
5655	- 0.08	- 20.1	- 265.4
5600	- 0.13 <sup>+</sup>	- 32.8	- 432.0
5540	- 0.20	- 50.3	- 663.5
5470	- 0.31 <sup>-</sup>	- 78.0	- 1028
5435	- 0.37	- 93.1	- 1228
5330	- 0.54 <sup>+</sup>	- 135.8	- 1792
5240	- 0.72 <sup>-</sup>	- 181.1	- 2389
5198	- 0.73	- 183.7	- 2422
5160	- 0.72 <sup>-</sup>	- 181.1	- 2389
5080	- 0.60 <sup>-</sup>	- 150.9	- 1991
5070	- 0.55 <sup>-</sup>	- 138.4	- 1825
5030	- 0.10	- 25.1	- 331.8
5010	- 0.21 <sup>+</sup>	+ 52.8	+ 696.8

observed are reviewed in the accompanying tables; Fig. 7, moreover, gives a graphical representation of these numbers.

The specific rotation becomes equal to zero for a wave-length of 5025 A.U.; from Fig. 7 the shift of the curve with respect to the corresponding curve of the *iodide* may be seen, as a consequence of the rotatory influence of the *dextrogyratory bromocamphorsulphonic acid* contained in it.

In the case of the *dextrogyratory* antipode, the measurements were made only between 5140 and 6290 A.U., as a consequence of the greater concentration used here. The part of the dispersion-curve determined, however, proves convincingly, that the curve is completely analogous to that of the *levogyrotary* component, being its mirror-image.

The curve of the rotatory dispersion in the case of the *iodide* is also

Observed, specific and molecular Rotations of the Solutions of levogyratory $\left\{ \text{Co} \begin{matrix} (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{matrix} \right\} \text{I}_3$ .			
The solution contained 0.1230 gram iodide in 100 ccm. solution. The length of the tube was: 1 dm.			
Wave-length in A. U.:	Rotation $\alpha$ observed:	Specific Rotation $[\alpha]$ :	Molecular Rotation $[M]$ :
6850	— 0.02 <sup>+</sup>	— 16.3	— 124.2
6445	— 0.01 <sup>+</sup>	— 11.4	— 87.0
6258	— 0.01 <sup>3</sup>	— 10.6	— 80.7
6092	— 0.02	— 16.3	— 124.2
5940	— 0.04 <sup>—</sup>	— 32.5	— 248.5
5783	— 0.08 <sup>—</sup>	— 65.0	— 497.0
5655	— 0.14	— 113.8	— 869.6
5540	— 0.20	— 162.6	— 1242.3
5435	— 0.29	— 235.1	— 1801.3
5330	— 0.39	— 317.0	— 2422.4
5240	— 0.48	— 389.9	— 2981.4
5160	— 0.52	— 422.8	— 3230
5070	— 0.48 <sup>—</sup>	— 388.8	— 2981.4
5005	— 0.33	— 268.3	— 2050
4935	— 0.07 <sup>—</sup>	— 56.9	— 434.8
4865	+ 0.23	+ 186.9	+ 1429
4830	+ 0.58	+ 471.6	+ 3603
4755	+ 0.82	+ 666.8	+ 5093
4635	+ 0.97	+ 788.6	+ 6025

typically abnormal: between 4635 and 4910 A.U. the solutions are dextro- (or levo-)-rotatory for the smaller wave-lengths, levo- (resp. dextro-)-gyratory for the greater wave-lengths. The rotation becomes zero for  $\lambda = 4910$  A.U.; a COTTON-effect is present, as can be seen immediately from the curve in Fig. 7. The maximum specific rotation is in the case of the levogyratory antipode situated in the vicinity of 4500 A.U. and has the value of about  $+840^\circ$ , while the greatest levo-rotation, occurring at 5160 A.U. is numerically only half this value, i.e.  $-426^\circ$ .

Although this dispersion-curve is not determined in its full extension,

Observed specific and molecular Rotations of a Solution of dextrogyratory $\left\{ \text{Co} \begin{matrix} (\alpha\text{-Phen}) \\ (\text{Eine})_2 \end{matrix} \right\} \text{I}_3$ .			
The solution contained 0,2700 gramme of the salt in 100 ccm. of the solution. The length of the tube is 1 dm.			
Wave-lengths in A. U.:	Rotation $\alpha$ observed:	Specific Rotation $[\alpha]$ :	Molecular Rotation $[M]$ :
6290	0.03	+ 11.1	+ 84.9
6090	0.05	+ 18.5	+ 141.5
5940	0.09	+ 33.3	+ 254.7
5783	0.18	+ 66.8	+ 509.4
5655	0.31	+ 114.8	+ 877.2
5540	0.45+	+ 166.8	+ 1273
5435	0.61	+ 225.9	+ 1726
5330	0.84	+ 311.1	+ 2377
5240	1.04	+ 385.2	+ 2943
5160	1.16	+ 429.6	+ 3282
5140	1.13+	+ 418.5	+ 3197

there is no doubt about the fact, that it is in Fig. 7 the mirror-image of the first one, the almost pure component therefore really being present here.

For the purpose of comparison, the dispersion-curve for *d*- (or *l*-) *Triethylenediamine-Cobaltic-iodide*<sup>1)</sup> is also drawn in Fig. 7. This comparison shows that the substitution of one of the molecules  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$  in the complex ion by one molecule of the also symmetrically built molecule of  *$\alpha$ -Phenanthroline* has the result that, notwithstanding the general character of the original dispersion-curve is preserved, there is a slight shift of the zero-rotation from 4845 A. U. towards 4910 A.U., besides an increase of both rotation-maxima, which, moreover, are shifted in *opposite* directions: the one maximum being shifted from 4735 A.U. and a value of  $412^\circ,5$  towards 4500 A.U. approximately and a value of  $840^\circ$ , while the other is moved from 5100 A.U. and  $406^\circ$  towards 5160 A.U. and  $426^\circ$ . The latter change is, however, insignificant in comparison with that of the other maximum, as a consequence of which *the originally almost symmetrical dispersion-curve of*

<sup>1)</sup> The new measurements of the values necessary for the construction of the curve in Fig. 7, were made by my former assistant, Mr. P. KOETS.

the highly symmetrical Triethylenediamine-Cobalti-complex is now distorted into a distinctly unsymmetrical curve. The substitution within the complex ion influences therefore chiefly the first rotation-maximum, corresponding to the shorter wave-lengths; on the contrary, the second

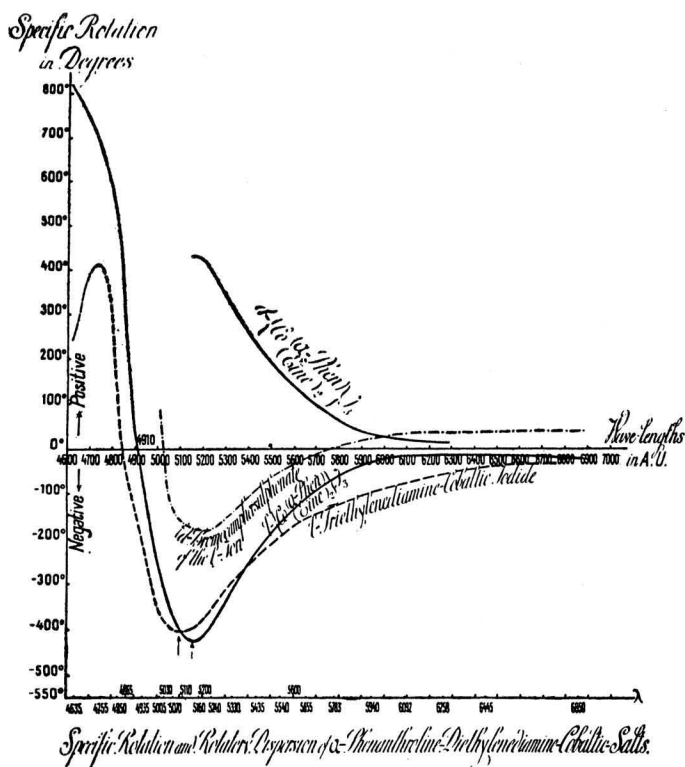


Fig. 7.

maximum, as well as the zero-point of the curve are evidently influenced only to an unappreciable extent.

§ 9. Several tentatives were made also to obtain the optically-active salts or their derivatives in a well crystallized form, with the purpose to control with these crystals the validity of PASTEUR'S law concerning the relation between optical activity and enantiomorphism of crystalline forms also in this case; moreover, after isolation of the enantiomorphous individuals it would then be possible to determine the specific rotation in solution once more. For the isolation of the completely pure optically-active *iodides* is always somewhat difficult, because these iodides were not obtainable in good individual crystals, so that no absolute certainty existed, that no trace of admixed racemic iodide made the rotation appear too low. With respect to the formerly observed crystallizing power of the racemic *chlorate*, the choice was first of all fixed upon the optically-active *chlorates* for this purpose; later also the *sulphates* and the *perchlorates* were prepared. The different optically-active fractions of

the *iodides*, therefore, were converted into the corresponding *chlorates*, *sulphates* or *perchlorates* by means of the *silver-salts* of these acids, and the solutions thus obtained were allowed to crystallize very slowly during evaporation at room-temperature. Soon it became clear, however, that it was much more difficult to obtain good, measurable crystals of these active salts, than such was the case with the racemic substances, as a consequence of the much greater solubility of the first. Of the *sulphate* hitherto no measurable crystals could be obtained; the *perchlorates* crystallize badly, but it could be stated, that they were triclinic-pedial.



From an aqueous solution this salt is deposited in the shape of very small, orange-yellow needles or short, rectangularly bordered prisms, which evidently contain  $2 \text{H}_2\text{O}$  ( $=5,4\%$ ).

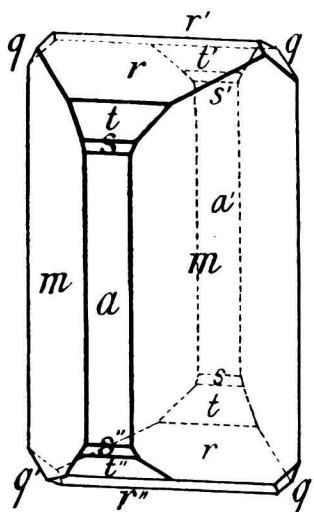


Fig. 8.

Monoclinic; probably *sphenoidal* and pseudo-rhombic.

$$a : b : c = 1,5133 : 1 : 0,4433;$$

$$\beta = 87^\circ 55'.$$

*Forms observed:*  $m = \{110\}$ , well developed and strongly lustrous;  $a = \{100\}$ , commonly narrower than  $m$ , excellently reflecting, often its faces developed equally in height and in breadth as highly developed faces,  $m$  in that case being much narrower;  $r = \{101\}$  and  $r' = \{\bar{1}01\}$ , almost equally broad and yielding good reflections;  $t = \{301\}$  and  $t' = \{\bar{3}01\}$ , narrower than  $r$ , but giving sharp images;  $s = \{501\}$  and  $s' = \{\bar{5}01\}$ , much narrower than  $r$  and  $t$ , but reflecting very well;  $q = \{031\}$ , often

absent, sometimes observable as small truncation of the ends of the prismatic crystals and only approximately measurable. The habit is long-prismatic parallel to the  $c$ -axis or shorter, with flattening parallel to  $\{100\}$ . (Fig. 8).

Angular values :

Observed : Calculated :

$a : m = (100) : (110) =^*$	56°	31½'	—	—
$a' : s' = (\bar{1}00) : (501) =^*$	34	59	—	—
$a' : r' = (\bar{1}00) : (\bar{1}01) =^*$	75	36	—	—
$s' : r' = (\bar{5}01) : (\bar{1}01) =$	40	35	40°	37'
$r' : r = (\bar{1}01) : (101) =$	32	38	32	38½
$r : s = (101) : (501) =$	37	36	38	6½
$a : s = (100) : (501) =$	34	8	33	39



Angular values :	Observed :	Calculated :
$a' : t = (\bar{1}00) : (\bar{3}0\bar{1}) =$	47 37	47 31
$m : q = (110) : (031) = ca.$	47°	47 16
$m : m = (110) : (\bar{1}\bar{1}0) =$	66 57	66 57
$m : t = (110) : (301) =$	68 14	68 8
$c : q$ (plane angle) $= ca.$	53°	53 2½

No distinct cleavage was observed.

On  $\{100\}$  there is in no situation complete extinction, as a consequence of a strong conical refraction. Perpendicular to  $\{100\}$  one of the optical axes emerges. The plane of the optical axes is  $\{010\}$ ; inclined dispersion. No appreciable dichroism is observable.

§ 11. The production of *Triethylenediamine-Cobaltic-complexes* during the reaction between mono- and bivalent amines in solution on salts of the *Diethylenediamine-chloro-aquo-Cobaltic-ion*, as mentioned above, was also stated in analogous reactions with other mono- and bi-valent amines like those already described; the phenomenon even appeared to occur also, when *Diethylenediamine-dihalogeno-Cobaltic-salts* (*Praseo-salts*) were used in these reactions<sup>1)</sup>. Thus e. g. in the reaction between *l-Menthylamine* and the corresponding *chloro-aquo-Cobaltic* salt and after treating the reaction-products with *bariumchloride*, big crystals with the colour of the *Luteo-cobaltic-salts* were obtained, possessing the form of (Fig. 9).

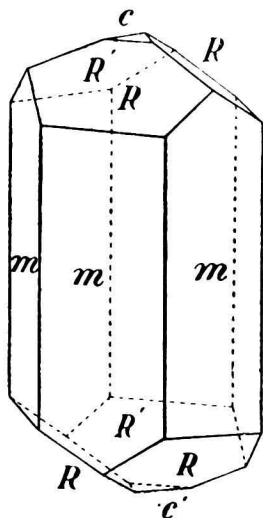


Fig. 9.

*Ditrigonal-scalenohedral.*

$$a = 107^\circ 34'; a : c = 1 : 0,9758.$$

*Forms observed:*  $m = \{10\bar{1}0\} = \{2\bar{1}\bar{1}\}$ , large and very lustrous;  $R = \{10\bar{1}1\} = \{100\}$ , well developed and yielding good images;  $c = \{0001\} = \{111\}$ , also well developed and sharply reflecting. The crystals are often peculiarly distorted and tabular parallel to faces of  $m$ .

Angular values :	Observed :	Calculated :
$c : R = (0001) : (10\bar{1}1) =$	*87° 58'	—
$R : R = (10\bar{1}1) : (\bar{1}\bar{1}01) =$	64 29	64° 23'
$m : R = (10\bar{1}0) : (10\bar{1}1) =$	52 2	52 2
$m : R = (0\bar{1}\bar{1}0) : (10\bar{1}1) =$	72 6	72 5
$m : m = (10\bar{1}0) : (0\bar{1}\bar{1}0) =$	59 58	60 0

<sup>1)</sup> Comp.: F. M. JAEGER and P. KOETS, These Proceed. 29, (1926), p. 67.

On *m* distinctly dichroitic: for vibrations parallel to the *c*-axis pale orange-red, for those perpendicular to them: orange. Optically-uniaxial without circular polarisation; negative. Notwithstanding the deviating habit, these crystals are identical with those of  $\{\text{Co}(\text{Eine})_3\} \text{Cl}_3 + 3 \text{H}_2\text{O}$ , formerly described<sup>1)</sup>. The determinations of  $\text{H}_2\text{O}$  and  $\text{Cl}$  were also in full agreement with this constitution, no doubt whatsoever being possible with respect to the said identity.

§ 12. The same fact was stated with respect to the *Chlorosulphates*, which are produced, if racemic or levogyrotory *Pentane-2-4-diamine* or the corresponding *meto*-base are heated with the *chloro-aquo-salts* in aqueous solution in sealed glass-tubes at  $110^\circ \text{C}$ . during six hours. In this case there is deposited a salt of typically rhombohedral form (Fig. 10), as described here.

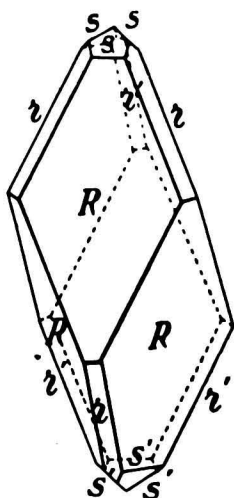


Fig. 10.

*Ditrigonal-scalenohedral.*

$$a = 50^\circ 36'; a : c = 1 : 3,0544.$$

*Forms observed:*  $R = \{100\} = \{10\bar{1}1\}$ , strongly predominant and well reflecting;  $r = \{110\} = \{01\bar{1}2\}$ , as narrow truncation of the polar edges of  $R$ , yielding mostly faint, rarely also sharper reflections;  $s = \{211\} = \{\bar{1}014\}$ , small, but well measurable.

*Angular values:*                      *Observed:*    *Calculated:*

$s : s' = (211) : (121) = 69^\circ 53'$	—
$R : R = (100) : (0\bar{1}0) = 67 \ 13$	$67^\circ 9'$
$R : r = (100) : (110) = 56 \ 23\frac{1}{2}$	$56 \ 25\frac{1}{2}$

No distinct cleavage was present.

Optically-uniaxial; negative, without circular polarisation.

§ 13. The optically-active *Pentane-2-4-diamines* necessary for these experiments were obtained from the racemic base by means of the *acid d-tartrates*. To a solution of the racemic base, the strength of which was carefully determined, a solution of dextrogyrotory *tartaric acid* was added in proportion of 2 molecules of the acid to 1 molecule of the base. When the solution is sufficiently concentrated on the waterbath, crystallization sets in; during the evaporation on the waterbath a certain quantity of *acetone* is added to the solution, by which evidently the evaporation of the base set free by a slow dissociation of the *bitartrate*, is somewhat retarded (KOETS), while also the solubility of the *bitartrate* in a mixture of water and acetone is less than in water alone. After recrystallization

<sup>1)</sup> F. M. JAEGER, Rec. d. Trav. Chim. d. Pays-Bays, loco cit.

stallizing twelve times, the specific rotation of the salt appeared to remain constant:  $[a]_D = +26^\circ$ .

*Analysis:* 5,07 m.G. give 0,304 ccm.  $N_2$  of  $16^\circ C.$  and a pressure of 763 mM.; this corresponds to 7,11 % N, while 6,97 % N is calculated.

After the *tartaric acid* is eliminated by means of *KCl*, the base was set free from the hydrochloride obtained by means of solid *KOH*; the less soluble *bitartrate* gives in this way the *levo-gyratory* base.

*Crystalform of l-Pentane-2-4-diamine-bi-d-tartrate:*  $C_5H_{10}(NH_2)_2, 2C_4O_6H_6.$

This substance crystallizes in small, transparent, colourless and highly lustrous crystals of varying habitus. From warm solutions individuals are deposited having the shape of Fig. 11a. From cold solutions, however, the crystals of Fig. 11b and 11c are deposited, which apparently do not show any trace of hemihedrism. The vertical zone is only approximately measurable, because of a fine striation of the already very narrow faces, so that multiple reflections occur.

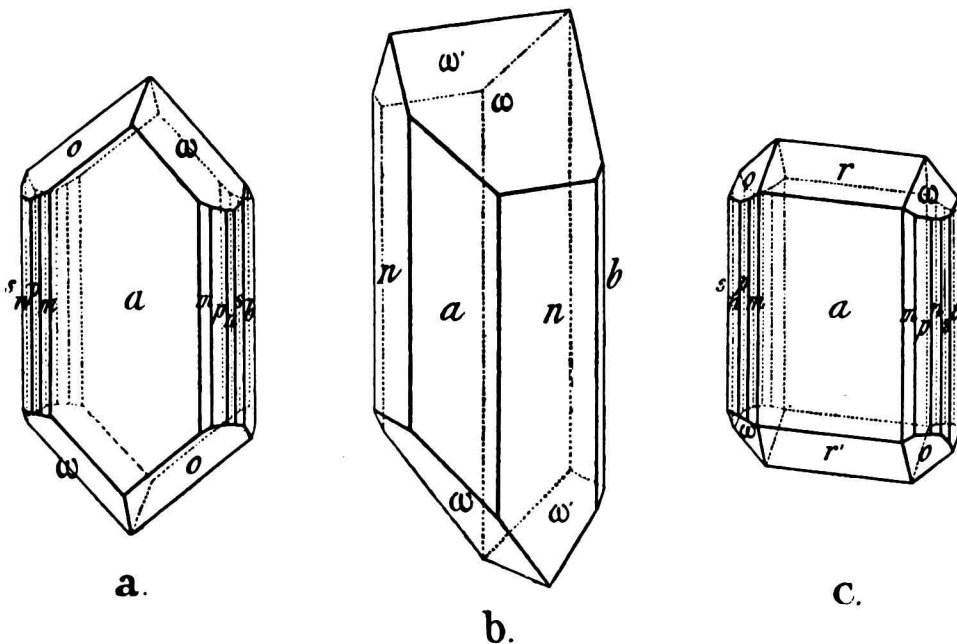


Fig. 11.

*Rhombic-bisphenoidal.*

$$a : b : c = 1,3518 : 1 : 0,9750.$$

*Forms observed:*  $a = \{100\}$ , mostly broadest of all, rarely narrower, however, than  $n = \{110\}$ ; when all prisms are present,  $n = \{110\}$ ,  $m = \{310\}$  and  $p = \{210\}$ , are all almost equally broad and highly lustrous;  $s = \{140\}$  and  $b = \{110\}$ , however, are very narrow and dull; these forms

are often absent. Furthermore:  $\omega = \{111\}$  and  $o = \{\bar{1}\bar{1}\bar{1}\}$ , mostly equally well developed and physically only unappreciably different, both yielding sharp images. Sometimes only  $\omega = \{111\}$  is present as a typical bisphenoid. Further:  $r = \{101\}$  and  $t = \{701\}$ , rarely present otherwise than with crystals of type 11c, but in that case large and very lustrous;  $q = \{011\}$ , well developed, often absent, but always yielding good reflections;  $c = \{001\}$ , mostly absent and extremely narrow.

<i>Angular values :</i>	<i>Observed :</i>	<i>Calculated :</i>	
$\omega : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$*77^\circ$	$26\frac{1}{2}$	—
$a : \omega = (100) : (111) =$	$*63$	$38\frac{1}{2}$	—
$\omega : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	52	43	$52^\circ$ 43'
$m : \omega = (310) : (111) =$	48	35	48 34
$\omega : b = (111) : (010) =$	51	17	51 17
$a : m = (100) : (310) =$	24	15	24 $15\frac{1}{2}$
$m : p = (310) : (210) =$	9	44	9 48
$p : n = (210) : (110) =$	19	30	19 27
$n : s = (110) : (140) =$	23	51	23 $42\frac{1}{2}$
$s : b = (140) : (010) =$	12	35	12 47
$n : n = (110) : (\bar{1}\bar{1}\bar{1}) =$	73	2	72 59
$a : n = (100) : (110) =$	53	31	53 31
$n : \omega = (110) : (111) =$	40	39	40 $40\frac{1}{2}$
$\omega : \omega = (111) : (\bar{1}\bar{1}\bar{1}) =$	98	42	98 39
$n : \omega = (110) : (\bar{1}\bar{1}\bar{1}) =$	76	31	76 $36\frac{1}{2}$
$\omega : q = (111) : (011) =$	26	$18\frac{1}{2}$	26 15
$\omega : \omega = (111) : (\bar{1}\bar{1}\bar{1}) =$	128	47	128 43
$r : \omega = (101) : (111) =$	38	47	38 43
$r : o = (101) : (\bar{1}\bar{1}\bar{1}) =$	73	59	73 48
$r : r = (101) : (\bar{1}\bar{0}\bar{1}) =$	69	20	69 22
$r : t = (101) : (201) =$	19	42	20 35

No distinct cleavability was found.

On  $\{100\}$  and in the zone of the  $c$ -axis everywhere normal extinction.

The plane of the optical axes is  $\{001\}$ ; on  $\{100\}$  both branches of the hyperbola are visible in convergent polarized light.

§ 14. On using now this *l*-Pentane-2-4-diamine in the fore-said experiments, also crystals were met with, which showed only  $R = \{100\}$  or only  $R$  and  $c$  combined; if the *meso*-base was used, crystals were found, which showed  $R$ ,  $r$  and  $s$ . But in both cases the angular values were completely analogous. As already mentioned above, the same crystal-forms were met with in the case, that  *$\alpha$ -Phenanthroline* reacts with the *chloro-aquo*-salt; they are all identical with those of the *chlorosulphate*

of the *Triethylenediamine-Cobaltic-ion*, which salt has a constitution represented by the formula:  $\left\{ \text{Co} (\text{Eine})_3 \right\} \left\{ \begin{matrix} \text{Cl} \\ (\text{SO}_4) \end{matrix} \right\} + n\text{H}_2\text{O}$ , in which  $n$  is most probably equal to 3. Analysis gave no quite reliable results, probably as a consequence of a partial decomposition of the salt on heating or by the admixture of accessory products (*trichloride* and other *chlorosulphates*), which could not be completely eliminated by recrystallisation.

If all these *chlorosulphates* be converted into the corresponding *iodides* by means of *NaI*, the salts obtained appear to be all identical, notwithstanding the more or less accidental deviations in their habitus. They all represent the *iodide* of the *Triethylenediamine-Cobaltic-ion*: rhombic-bipyramidal;  $a : b : c = 0,8538 : 1 : 0,8625$  or values only slightly different from this; forms:  $o \{111\}$ ,  $c = \{001\}$ ;  $\omega = \{221\}$ ;  $q = \{041\}$ ; angular values:  $c : o = 52^\circ 56'$  till  $53^\circ 5'$ ;  $o : o = 62^\circ 27'$  till  $62^\circ 48'$ ;  $o : \omega = 15^\circ 58'$  till  $16^\circ 11'$ ;  $o : o' = 74^\circ 39'$  till  $75^\circ 3'$ ; etc. Also the optical orientation is in all these cases identical. Their constitution is in all cases:  $\{\text{Co}(\text{Eine})_3\} \text{I}_3 + 1\text{H}_2\text{O}$ . It is remarkable, that in the last mentioned reactions these *Triethylenediamine-Cobaltic-derivatives* seem to represent indeed the *principal* product of the reaction; the bases used are only present in the last mother-liquids, which do not crystallize very well.

Also if *d-*, *l-*, or *rac. a-Propylenediamine* in aqueous solution react with the *chloro-aquo-salt*, always the same *chlorosulphates*, respectively *iodides* are obtained. If really the normal reaction-products shall be obtained in such cases, the only feasible method consists in the reaction between the *anhydrous* bases (or their monohydrates) and the corresponding *Praseo-salts* at *low* temperatures, a method already followed by PFEIFFER, GRASSMANN and PIETSCH<sup>1)</sup> in the case of *a-Propylenediamine*. Indeed, in this way the desired *a-Propylenediamine-diethylenediamine-Cobaltic-salts* were obtained, showing the properties already mentioned by the said authors. However, it was not possible hitherto to obtain these salts in a form, suitable for crystallographical research; in most cases only fine needles grouped in rosettes were obtained in this way.

The investigations of the products obtainable by the reaction between the *anhydrous pentane-diamines* and the *praseo-Cobaltic-salts* are meanwhile continued by us.

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<sup>1)</sup> P. PFEIFFER, TH. GRASSMANN and H. PIETSCH, Zeits. f. anorg. Chemie, **58**, 301, (1908).