

Chemistry. — *Investigations on the Complex Salts of the Racemic and Optically active Cyclohexanediamines with trivalent Cobaltum and Rhodium. III. Tri-Cyclohexanediamine Salts of trivalent Cobaltum.*

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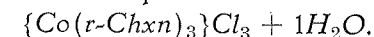
§ 1. The racemic *cyclohexanediamine* as well as its optically active components¹⁾ can be used in the preparation of the *cobaltic* salts; the corresponding products will be indicated in this paper as (*r-Chxn*)-, (*d-Chxn*)- or (*l-Chxn*) salts respectively. The preparation of the *tri-cyclohexanediamine* salts of this series always has to occur via the corresponding *praseo*- (or *violeo*)-salts of the type: $\left\{ \text{Co} \begin{matrix} (\text{Chxn})_2 \\ \text{Cl}_2 \end{matrix} \right\} \text{Cl}$. The preparation of the latter is the same, whether one starts from the racemic or from the optically active bases. 30 Grammes of hydrated *cobaltous chloride*: $\text{CoCl}_2 + 6\text{H}_2\text{O}$ are dissolved in 110 cm³ water and the solution cooled to 15° C. It then is brought into a big ERLLENMEYER-flask of 3 liters volume and mixed with 27,6 grammes of *cyclohexanediamine*: a pink precipitate is formed which in contact with the air rapidly assumes a dark brown colour. Under continuous shaking of the liquid now 240 cm³ of a 10 % solution of hydrogen peroxide are very slowly added from a dropping funnel; the temperature of the mixture gradually rises to about 40° C., while the colour of the liquid turns into a dark brown and a rather voluminous froth is continuously formed, filling the whole space of the vessel. After all hydrogen peroxide has been added and the original precipitate has completely vanished, a reddish-brown, clear solution remains, which is left standing for some hours and then is heated on the waterbath for the purpose of completing the reaction and destroying the peroxide still present. Sometimes a small quantity of a pale pink precipitate is formed thereby, which, however, disappears on addition of 450 cm³ of strong (1,19) hydrochloric acid. The acid solution now is evaporated to dryness on the water-bath, the dark green residue thus obtained repeatedly treated with absolute alcohol, and the alcoholic solutions each time completely evaporated. The final residue then is dried in a vacuum-exsiccator over CaO during several days, until all traces of hydrochloric acid still present are removed as completely as possible. The viscous, dark green mass then is repeatedly extracted by means of boiling absolute alcohol, the bluish-green extract filtered and evaporated, till a syrupy green mass is obtained, which is dried in vacuo over CaO. The *praseo*-salt (97 % of the theoretical yield) thus obtained is a dark green, *very hygroscopic* mass, which cannot be obtained in an absolutely pure state, nor in a well crystallized form.

¹⁾ F. M. JAEGER and L. BIJKERK, these Proceed., 40, 12 (1937).

During the oxidation, moreover, about 5—6 % of a dark brown, peculiarly smelling organic substance is generated, which also dissolves in the alcohol used. A black residue, obtained on filtering off the alcoholic extracts, is repeatedly washed with absolute alcohol and then dissolved in an excess of boiling water; it chiefly consists of the corresponding *tri-cyclohexanediamine* salt simultaneously formed, which, after filtering and evaporating, is obtained from its aqueous solution and can finally be recrystallized from boiling water. In this way 31 grammes of the *praseo*-compound and 3 grammes of the *tri-cyclohexanediamine* salt were isolated. The green *praseo*-salt dissolves in water to a reddish solution, most probably because of its being immediately transformed into the *diaquo*-salt.

§ 2. The corresponding *tri-cyclohexanediamine-cobaltic chloride* can be obtained from the green mass by boiling its solution in water during three hours with the calculated quantity of the base at a reflux-cooler provided with a tube filled with sodium- and calcium hydroxides. As the salt formed is only sparingly soluble, a sufficient quantity of water must be added, so as to prevent too much bumping of the boiling liquid.

The warm salt-solution then is filtered off from a little of a black residue, evaporated on the water-bath, and the *chloride* obtained recrystallized from boiling water. The salt crystallizes in beautiful, fine needles of the composition:



Analysis: 20,2 % Cl; 15,91 % N; 3,37 % H₂O; calculated: 20,27 % Cl; 15,99 % N; 3,42 % H₂O.

This *racemic compound*: $\text{r-}\left\{ \text{Co}(\text{Chxn})_3 \right\} \text{Cl}_3 + 1\text{H}_2\text{O}$ crystallizes from a hot aqueous solution, on cooling, in long, yellow- or orange-red, lustrous, but very brittle thin needles, which usually only show an incomplete number of terminal faces. They are *ditetragonal-bipyramidal*; this was, moreover, corroborated by a LAUE-diagram on {001}. The axial ratio is: $a : c = 1 : 0,7212$. Some crystals were measured by means of the theodolite-goniometer (by Mr. TER BERG), the others by the aid of the usual one-circle-goniometer.

Forms observed: $a = \{100\}$, well developed and lustrous; $r = \{101\}$, small, but yielding good reflections; $p = \{211\}$, well developed, although mostly present with only part of its faces; $s = \{443\}$, small, giving good reflections; $t = \{337\}$, very narrow, but well measurable. The habitus is long-prismatic parallel to {100}. (Fig. 1).

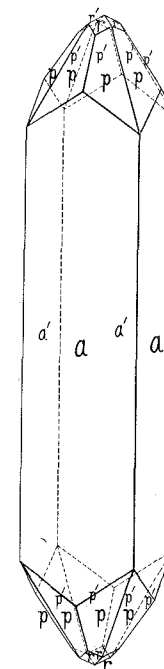


Fig. 1. *Crystal form of racemic*
 $\left\{ \text{Co}(\text{Chxn})_3 \right\} \text{Cl}_3 + 1\text{H}_2\text{O}$

Angular Values:	Observed:	Calculated:
$a:r = (100):(101) = *54^\circ 12'$		—
$r:r = (101):(011) = 48\ 34$		$48^\circ 52'$
$a:p = (100):(211) = 40\ 24$		40 31
$a:p = (010):(211) = 67\ 28$		67 39
$c:p = (001):(211) = 57\ 32$		58 12
$p:p = (211):(121) = 30\ 48$		31 11
$s:t = (443):(337) = 29\ 35$		30 3
$s:c = (443):(001) = —$		53 40
$t:t = (337):(\bar{3}\bar{3}\bar{7}) = 47\ 38$		47 14
$s:a = (443):(010) = 55\ 20$		55 $16\frac{1}{2}$
$c:r = (001):(101) = 35\ 48$		35 48

A distinct cleavability could not be observed.

§ 3. The corresponding bromide: $\{\text{Co}(r\text{-Chxn})_3\}\text{Br}_3 + 1\text{H}_2\text{O}$ (with 2,69% H_2O ; calculated: 2,73%) is even less soluble than the chloride. Thusfar it could not yet be obtained in measurable crystals.

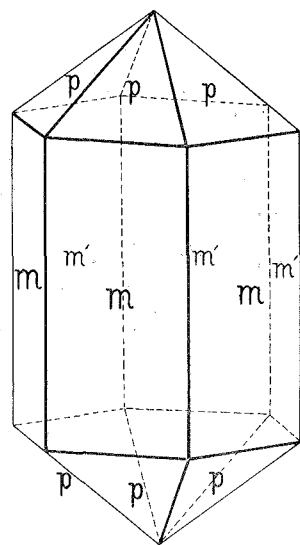


Fig. 2. Crystal form of $\{\text{Co}(r\text{-Chxn})_3\}(\text{NO}_3)_3 + 3\text{H}_2\text{O}$

The chloride, nitrate, chlorate and perchlorate of this series are rather badly soluble in cold, better in hot water; the greater part of the salts dissolved ordinarily falls out on cooling, but sometimes small, well developed crystals can be obtained from the very dilute mother-liquors, by very slow evaporation at room-temperature.

Measurable crystals were, in this way, obtained in the case of the nitrate, the chlorate and the perchlorate.

1. Tricyclohexanediamine-cobaltic nitrate: $\{\text{Co}(r\text{-Chxn})_3\}(\text{NO}_3)_3 + 3\text{H}_2\text{O}$ crystallizes in small orange-brown crystals (Fig. 2).

Hexagonal-bipyramidal.
 $a:c = 1:0,7834$.

Forms observed: $m = \{10\bar{1}0\}$, lustrous and well-developed; $p = \{10\bar{1}1\}$, yields sharp reflections. Short prismatic; no distinct cleavability was observed.

Angular Values:

$$m:m = (10\bar{1}0):(01\bar{1}0) = 60^\circ$$

$$m:p = (10\bar{1}0):(10\bar{1}1) = 47^\circ 52'$$

$$p:p = (\bar{1}\bar{1}01):(10\bar{1}1) = 39\ 12$$

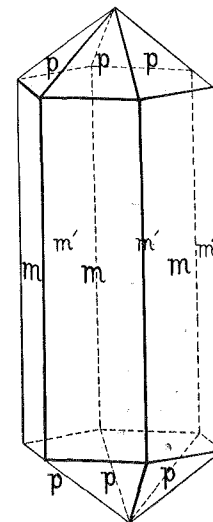
$$p:p = (10\bar{1}1):(\bar{1}011) = 84\ 16$$

$$m:p = (0\bar{1}10):(\bar{1}\bar{1}01) = 70\ 24$$

The angles observed and calculated do not differ more than about $4'$. The LAUE-diagram on $\{001\}$ proved to have no planes of symmetry, but the crystals are not piezo-electrical. Optically uniaxial, negative; according to Dr. TERPSTRA, for yellow light n_o is 1,5830, for green (Hg): 1,5863; for yellow light n_z is: 1,5744, for green light: 1,5783.

The analysis of the nitrate gave: 8,03% H_2O ; 19,8% N ; calculated: 8,4% H_2O ; 19,66% N .

2. Tricyclohexanediamine-cobaltic chlorate: $\{\text{Co}(r\text{-Chxn})_3\}(\text{ClO}_3)_3$ was also obtained from its solutions in small, prismatic needles, which,



according to Dr. TERPSTRA — who was kind enough to study these small individuals by the aid of the theodolite-goniometer — are of two different kinds. The one form (α) is hexagonal and evidently closely related to the analogously constituted nitrate and perchlorate; the other kind of crystals (β) is monoclinic-prismatic. Neither the chloride nor the nitrate, however, proved to be present in the preparation; whilst the β -chlorate, according to its analysis, is anhydrous, the α -chlorate, like the nitrate and perchlorate, most probably crystallizes with 3 molecules of water.

The hexagonal-bipyramidal α -form (Fig. 3) has the axial ratio: $a:c = 1:0,7653$.

Forms observed: $m = \{10\bar{1}0\}$, larger than α - $\{\text{Co}(r\text{-Chxn})_3\}(\text{ClO}_3)_3 + 3\text{H}_2\text{O}$ $p = \{10\bar{1}1\}$, yields bad reflections; the habitus is short-prismatic parallel to the c -axis. The analogy with the nitrate is seen from a comparison of the angular values:

$$m:m = (10\bar{1}0):(01\bar{1}0) = 60^\circ$$

$$m:p = (10\bar{1}0):(10\bar{1}1) = 48^\circ 32'$$

$$p:p = (\bar{1}\bar{1}01):(10\bar{1}1) = 38\ 40$$

$$p:p = (10\bar{1}1):(\bar{1}011) = 82\ 56$$

$$m:p = (0\bar{1}10):(\bar{1}\bar{1}01) = 70\ 40$$

Optically uniaxial, negative; the index n_o is greater than 1,566 and smaller than 1,580.

The specific weight of the crystals is: 1,471.

The β -form of the chlorate is monoclinic-prismatic; the axial ratio is: $a:b:c = 1,7282:1:1,5944$, with $\beta = 81^\circ 26\frac{1}{2}'$. (Fig. 4). In this position the c -axis appears to have the character of a morphologically pseudo-hexagonal axis of the crystals. The crystals are elongated parallel to the b -axis; they manifest the following forms: $a = \{100\}$ and $s = \{101\}$, also

$r = \{\bar{1}01\}$, about equally broad; but the reflections in this zone are rather bad and the angular values appreciably oscillate; $c = \{001\}$, very narrow;

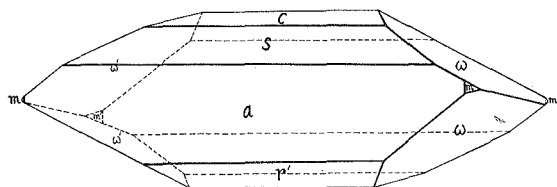


Fig. 4. Crystalform of β - $\{Co(r-Chxn)_3\}(ClO_3)_3$

$\omega = \{112\}$, well developed and yielding good images, like $o = \{\bar{1}11\}$, which, however, is much smaller than ω ; $m = \{110\}$, small and like $b = \{010\}$, mostly absent.

Angular Values:	Observed:	Calculated:
$b : \omega = (010) : (\bar{1}12) =$	$*52^\circ 45\frac{1}{2}'$	—
$b : o = (010) : (\bar{1}11) =$	$*38 32$	—
$a : s = (100) : (101) =$	$*42 42\frac{1}{2}$	—
$a : m = (100) : (110) =$	$59 41$	$59^\circ 40'$
$c : \omega = (001) : (\bar{1}12) =$	$44 21$	$44 21\frac{1}{2}$
$c : o = (001) : (\bar{1}11) =$	$64 39$	$64 39\frac{1}{2}$
$c : r = (001) : (\bar{1}01) =$	$46 36$	$46 36$

No distinct cleavability was observed.

On $\{\bar{1}01\}$ an axial image is visible, with the b -axis as second bisectrix.

The plane of the optical axes is perpendicular to $\{010\}$.

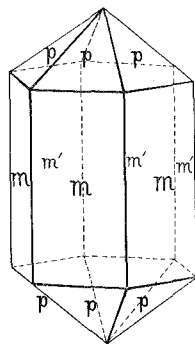


Fig. 5. Crystalform of r - $\{Co(Chxn)_3\}(ClO_4)_3 + 3H_2O$

3. The very sparingly soluble perchlorate: $\{Co(r-Chxn)_3\}(ClO_4)_3 + 3H_2O$ crystallizes in aggregations of very small, short prismatic crystals. They also are hexagonal-bipyramidal, with: $a : c = 1 : 0,7644$. The crystals manifest the forms: $m = \{10\bar{1}0\}$ and $p = \{10\bar{1}1\}$ and in their habitus exactly resemble those of the nitrate, chlorate, etc. (Fig. 5). Also the angular values, measured by means of the theodolite-goniometer, are perfectly analogous to those of the compounds mentioned:

Angular Values:	Observed:	Calculated:
$m : p = (10\bar{1}0) : (10\bar{1}1) =$	$*48^\circ 34'$	—
$p : p = (10\bar{1}1) : (0111) =$	$70 40$	$70 40\frac{2}{3}$

Optically uniaxial, negative the refractive index $n_o = 1,563$.
The specific weight of the crystals is: 1,550.

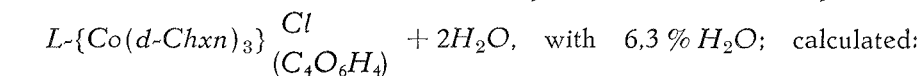
The analysis of the perchlorate yielded a water-content of 6,48 %, which is somewhat less than that required: 7,16 % for $3H_2O$.

The remarkable fact that the α -chlorate, the nitrate and the perchlorate have quite analogous crystalforms, — an analogy which borders on isomorphism, — illustrates the predominant influence of the symmetry of the complex ion upon the crystalform. This ion doubtlessly must have a hexagonal or trigonal symmetry and the presence of this senary or trigonal axis appears to be preserved even in some of the optically active salts, such as the d - and l -chlorides.

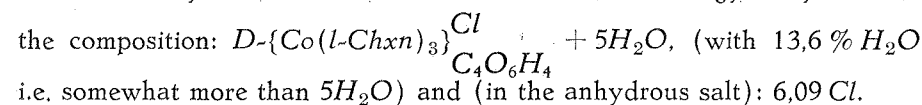
§ 4. In the analogous reactions, executed by using the *levo*- or *dextro*-gyratory components of the base, of course, the correspondingly constituted salts of these components are obtained; they will later on be described in detail. First, however, it seems necessary to describe the fission of the tricyclohexanediamine-cobaltic chloride into its optically active components, which can be readily performed by means of the chloro- d -tartrates. For this purpose a certain quantity of the racemic chloride was treated with the calculated amount of silver- d -tartrate and the solution, after removing the precipitate of $AgCl$, subjected to a fractional crystallization. The first, least soluble fractions chiefly consist of the pale, orange-yellow chloro- d -tartrate of the levogyratory ion, the last of the darker coloured, appreciably more soluble chloro- d -tartrate of the dextrogyratory salt.

In solution they immediately betray their abnormal rotatory dispersion and a COTTON-effect, thus giving proof of the fact, that a fission of the complex ion really has occurred.

The least soluble chloro- d -tartrate was proved to have the composition:



Occasionally the water-content of the needles was somewhat less and in better agreement with about 1,5 H_2O . It crystallizes in fine, yellow, prismatic needles, but up till now it could not be obtained in measurable crystals. The chloro- d -tartrate of the dextrogyratory ion has the composition:



$D-\{Co(l-Chxn)_3\} \frac{Cl}{(C_4H_4O_6)} + 5H_2O$ forms very small crystals, which were measured in the ordinary way and by means of the theodolite-goniometer by Dr. TERPSTRA. The angular values prove to oscillate strongly; divergencies of 2° are not rare.

The crystals are rhombic-bisphenoidal, with $a : b : c = 1,668 : 1 : 2,492$.
Forms observed:

$r = \{101\}$ and $q = \{011\}$, predominant; $m = \{110\}$, very small, but well measurable.

The habitus is variable, but mostly prismatic parallel tot the *b*-axis. (Fig. 6).

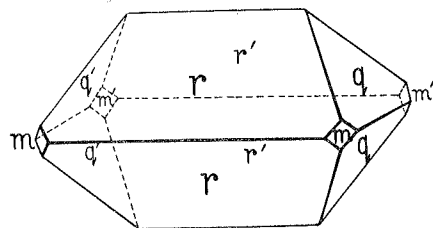


Fig. 6. Crystal form of
 $D-\left\{Co(l-Chxn)_3\right\}\frac{Cl}{C_4O_6H_4} + H_2O$

Angular Values:	Observed:	Calculated:
$q : q = (011) : (01\bar{1}) =$	$*43^\circ 44'$	—
$m : m = (110) : (\bar{1}10) =$	61 52	—
$r : r = (101) : (10\bar{1}) =$	67 44	$67^\circ 37'$
$m : r = (110) : (101) =$	64 45	64 43
$m : q = (110) : (011) =$	37 20	37 15

The *c*-axis has a pseudo-hexagonal character.
 The crystals are feebly but clearly piezo-electrical.

§ 5. The rotatory dispersion of the two *chloro-d-tartrates* proves to be somewhat variable with the higher or lower concentration of the solution used; but its general character is the same as that of the *chlorides* separated from them and is identical for both series of salts, but for the opposite algebraic signs. The *least* soluble *chloro-d-tartrate* shows *negative* rotations for wave-lengths greater than about 5890 Å; here the rotation becomes *zero* and then *positive* with a maximum in the vicinity of 5240 Å., subsequently diminishes to *zero* at about 5090 Å., then again becomes strongly *negative*, with a very steep minimum in the neighbourhood of 4730 Å. As will be demonstrated later on, this rotatory dispersion is characteristic of the complex ion containing three molecules of the *dextrogyratory* base. On the other hand, the behaviour of the *most* soluble *chloro-d-tartrate* and of the *chloride* isolated from it is the exact mirror-image of the first, in so far as the algebraic signs of the rotations are concerned: the curve of the rotatory dispersion of the *chloride* proves, on closer examination, to be the exact mirror-image of that observed with the salt into which three molecules of the *dextrogyratory* base have been introduced.

As an example of the rotatory dispersion observed with the *chloro-d-tartrates*, we here reproduce the results of the measurements of the specific rotations $[a]$ in the case of the *least soluble* fraction, for a solution containing 0,068 % of the (anhydrous) solute:

TABLE I.

$\lambda:$	$[a]:$	$\lambda:$	$[a]:$
		5340	+ 249.8
6980	- 51.4	5224	+ 271.8 M
6730	- 55.1	5126	+ 117.6
6480	- 58.7	5036	- 198.4*
6262	- 51.4	4950	- 411.4
6074	- 44.1	4861	- 999.0
5893	0	4793	- 1116.7
5735	+ 29.4*	4724	- 1146.0 m
5592	+ 88.2	4658	- 1116.7
5463	+ 191.0	4596	- 911.0
		4537	- 791.6

The typical aspect of the dispersion-curves in the two cases is represented in figure 7.

The fission of the racemic *bromide* occurs in an analogous way and with the same relations of the solubility of the two *bromo-d-tartrates*: the *chlorides* prepared from the corresponding bromides in all respects proved to be identical with those isolated from the least- and more-soluble *chloro-d-tartrates*. The only difference is that these *bromo-d-tartrates* are so sparsely soluble that the less soluble one is almost entirely precipitated in the reaction simultaneously with *Ag-bromide*; therefore, it must be isolated by repeatedly extracting the precipitate formed in a SOXLETT-apparatus by means of boiling water. After fractional crystallization of the solution on the water-bath, the last, darker red coloured mother-liquor chiefly contains the more soluble *bromo-d-tartrate*.

As to the dependence of the rotation and the shift of the zero-points on the concentration, it certainly must be attributed to the electrolytic decomposition of these *chloro-* and *bromo-d-tartrates* and the abnormal rotatory behaviour of the tartaric-acid ions in solution.

§ 6. From these *chloro-d-tartrates* the corresponding *chlorides* were set free by means of strong hydrochloric acid and then purified by recrystallization. The curve of the rotatory dispersion had, in each case, almost the same shape as in the figures A and B, and the absolute values of $[a]$ proved, within the limits of the experimental uncertainties, to be the same as those observed with the chlorides prepared by the direct intro-

duction of the dextro- and levogyrotory base respectively into the optically active *praseo-* (violeo-) salts (see Fig. 8). The zero-points of the curves

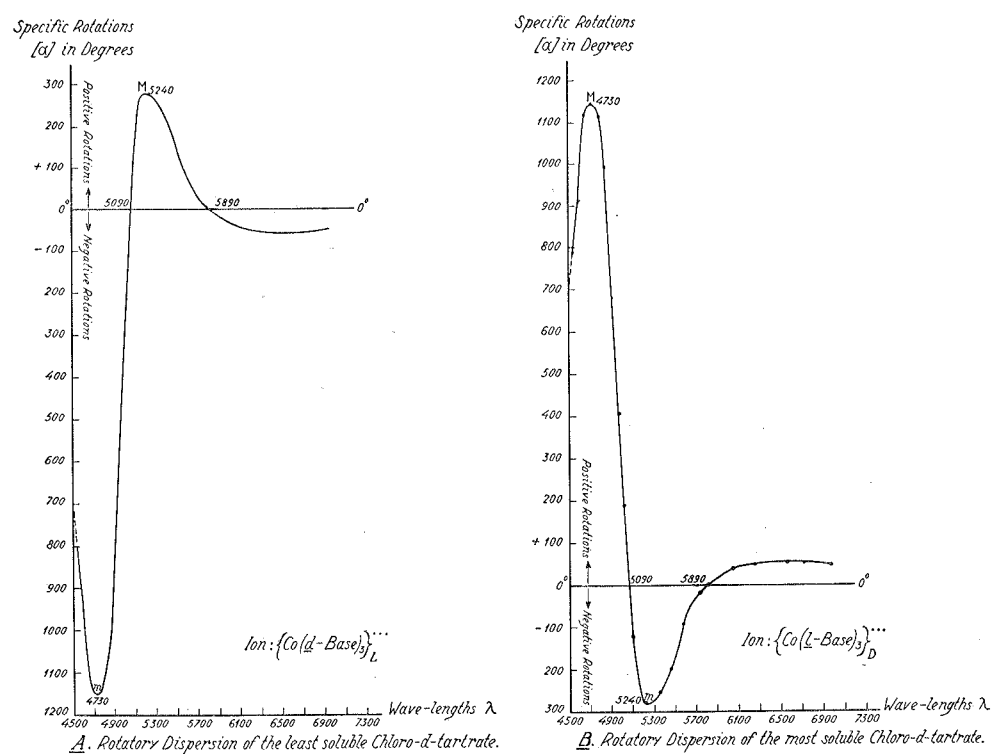


Fig. 7. Rotatory Dispersion of the two Chloro-d-tartrates of Tricyclohexanediamine-Cobaltic Chloride

for the pure chlorides appear, to be somewhat shifted towards the greater wave-lengths in comparison with those of the *chloro-d-tartrates*.

§ 7. The preparation of the *praseo*-salt and of the corresponding *tricyclohexanediamine-cobaltic chlorides* now was once more repeated, whilst this time the *optically active components* of the base were used for this purpose. The *praseo*-salts obtained proved, in their general properties, to be perfectly analogous to that of the inactive base: these hygroscopic, somewhat darker green salts, could not be obtained in a completely pure state and were not suited for analysis either. As in the previous case also in these, the formation of about 5—6 % of a black, aromatically smelling, accessory organic compound was observed, which most probably is generated by the oxidation of the base by the hydrogen peroxide used. These optically active *praseo*-salts are, when dissolved in water, also very rapidly transformed into the corresponding *chloro-aquo*, or *diaquo*-salts. Although no quantitative measurements of the rotation of these salts in

aqueous solutions could be made, as a consequence of their strong light-absorption even in small concentrations, it still could be stated that, for

instance, the salt $\left\{ \begin{array}{c} (\text{l-Chxn})_2 \\ \text{CoCl} \\ \text{H}_2\text{O} \end{array} \right\} \text{Cl}_2$ showed a positive rotation in the

red part, a negative rotation in the green part of the spectrum and that its rotatory dispersion already possessed a similar character as that observed with the corresponding *tricyclohexanediamine-cobaltic salts*.

These *praseo*-salts were finally transformed into the corresponding *tricyclohexanediamine-cobaltic chlorides* by heating them with one molecule of the *levo-* and *dextrogyrotory base* respectively.

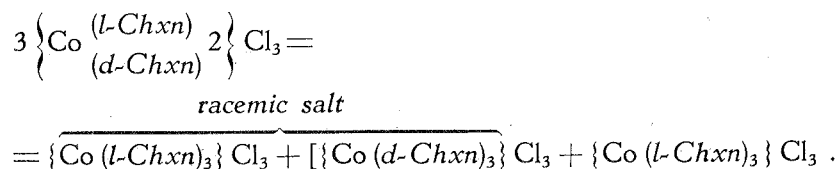
In this way it could be demonstrated that, on using, for instance, the *levogyrotory base*, a *tri-l-cyclohexanediamine-cobaltic chloride* was obtained, the rotation of which completely corresponded to that obtained by the earlier conversion of the *most soluble chloro-d-tartrate* into its chloride, as was described in the previous experiments. The use of the *dextrogyrotory base*, on the other hand, furnished the other antipode; if the algebraic sign of their rotations in the red part of the spectrum is arbitrarily taken as a standard, then the two salts can be represented by the following symbols of the complex ions present in them: $D\text{-}\{ \text{Co}(\text{l-Chxn})_3 \}^{\dots}$ and $L\text{-}\{ \text{Co}(\text{d-Chxn})_3 \}^{\dots}$. Other combinations of optically active constituents and of each of the optically active ionic configurations than the two mentioned are evidently *not* stable under these circumstances and are generated, amongst all imaginable combinations of this kind, solely by an exclusively *dissymmetrical* synthesis during the process of their formation.

In using the *inactive (d- + l-)* base and subsequently executing the fission of the racemic salt by means of *d-tartaric acid*, we previously obtained no other isomerides than just *the same* two antipodes mentioned: evidently they really represent the stable spatial configurations of these complex ions in the process involved. The observed relations are, therefore, in the present case exactly the same as they previously were stated by us¹⁾ in the case of the corresponding cobaltic salts of *cyclopentane-1-2-diamine*, where the ions $\{ \text{Co}(\text{l-Cptn})_3 \}^{\dots}$ and $\{ \text{Co}(\text{d-Cptn})_3 \}^{\dots}$, amongst all theoretically possible combinations, equally proved to be the *only really stable* ones formed in the reaction.

In this connection the following experiment still is of interest: The salt $\left\{ \begin{array}{c} (\text{l-Chxn})_2 \\ \text{Co} \\ \text{Cl}_2 \end{array} \right\} \text{Cl}$ in aqueous solution was boiled with one equivalent of the *dextrogyrotory base*. The dark-coloured solution was filtered off, during a short time boiled with *norite*, and the filtered, orange-red solution evaporated on the water-bath. First an orange-red salt crystallized in long, brittle needles, which proved to be *ditetragonal* and in solution manifested

¹⁾ F. M. JAEGER and H. B. BLUMENDAL, Zeits. f. Anorg. Chem., 175, 161 (1928).

no rotatory power. The crystals proved to be those of the *racemic* compound formerly described. From the last mother-liquors a more soluble fraction was obtained, which in solution showed the rotation characteristic of $D\text{-}\{Co(l\text{-}Chxn)_3\}Cl_3 + 4H_2O$. No other compounds than only these two were obtained. A salt of the composition: $\left\{Co \begin{matrix} (l\text{-}Chxn) \\ (d\text{-}Chxn) \end{matrix} \right\}_2 Cl_3$ was not present, but the latter, being *unstable*, is evidently decomposed according to the formula:



Just as in the case of the analogous *cyclopentane*-diamine salt, the salt with *l*- and *d*-molecules of the base simultaneously present within the complex ion *cannot exist* under these circumstances, but is immediately transformed into the salt with 3 molecules of the *levo*-, or of the *dextro*-gyratory base respectively. By special experiments it was proved that the combination of the hexagonal-pyramidal salts: $D\text{-}\{Co(l\text{-}Chxn)_3\}Cl_3 + 4H_2O$ and $L\text{-}\{Co(d\text{-}Chxn)_3\}Cl_3 + 4H_2O$ in equimolecular quantities gave indeed the *ditetragonal racemic salt* (+1H₂O). The latter, therefore, is a *combination* of the salts first mentioned. On making the *racemic* base react with an optically inactive salt, like *cobaltous chloride*, evidently not only the salts generated in the process are those of the *D*- and *L*-complexes, but *simultaneously a real fission of the originally optically inactive base into its antipodes is performed*, its optically active components being selectively directed into the *D*- or *L*-ions generated. This indeed is a very remarkable way of resolving a *racemic* substance into its optically active antipodes. The active bases afterwards can be set free from their complex salts by destruction and distillation with *KOH* and sodium formiate, as previously was already demonstrated in the case of the analogous *cyclopentane*-diamine salts.

§ 8. The rotatory dispersion of the two enantiomorphous salts is the same, except for the opposite algebraic signs of the rotations measured. Although even in this case some slight dependency of $[\alpha]$ on the concentration still seems to be present, the values measured yet prove to agree sufficiently to enable us to trace the true shape of the dispersion-curve. In the following table the data for the specific and molecular rotations of $D\text{-}\{Co(l\text{-}Chxn)_3\}Cl_3 + 4H_2O$ are collected:

The molecular rotations of the analogous compounds containing *d-cyclohexanediamine* have the same mean values, but with opposite algebraic signs.

The latter data of the molecular rotations $[M] \cdot 10^{-2}$ are graphically represented in Figure 8, curve I; they, therefore, correspond to the salt

isolated from the least soluble *halogeno-d-tartrates*. From this it appears that there are two wave-lengths: at about 5650 Å. and at 5126 Å. respec-

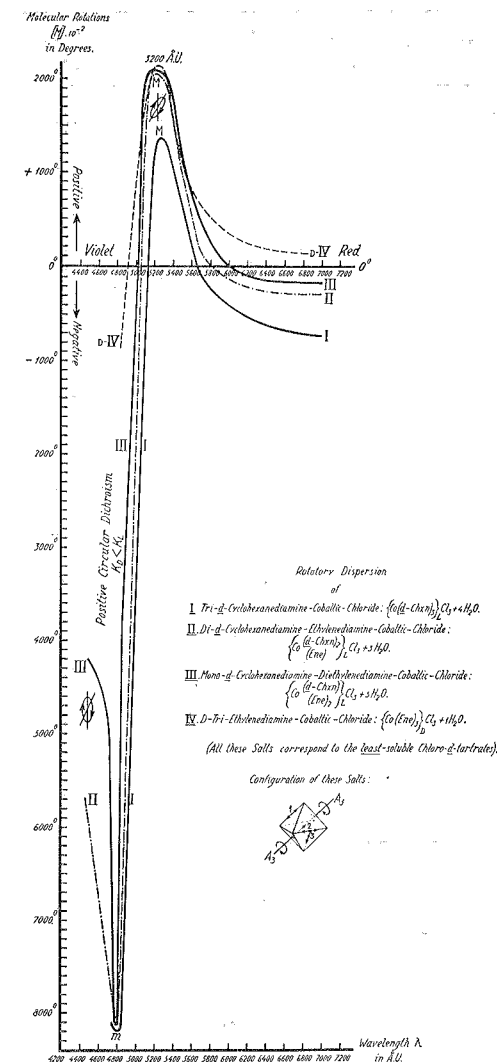


Fig. 8. Rotatory Dispersion of the Complex Cobaltic Chlorides with 3 molecules of *d*-Cyclohexanediamine and of those with *d*-Cyclohexanediamine and 1, 2 and 3 molecules Ethylendiamine respectively.

tively, — where the rotation of the solutions becomes zero; a *maximum* (*minimum* with the other antipode) is present at $\lambda = \text{ca. } 5300 \text{ \AA.}$ and a very steep *minimum* (*maximum* with the other antipode) in the vicinity of 4800 Å. Between 4800 and 5300 Å. the absorption-band shows a strong COTTON-effect of positive character.

§ 9. On comparing the molecular rotations with those of the corresponding salts of *cyclopentane-1-2-diamine*, attention must be drawn to the

TABLE II.
Specific and Molecular Rotations of $D\text{-}\{Co(l\text{-}Chxn)_3\}Cl_3 + 4H_2O$.

Wave-length λ in Å:	Specific Rotation $[\alpha]$ (mean values):	Mean Molecular Rotations $[M] \cdot 10^{-2}$:
6980	125.6	+ 728°
6730	119.4	+ 692
6480	114.9	+ 666
6262	109.0	+ 632
6074	94.5	+ 548
5893	80.9	+ 469
5735	25.7	+ 149
5592	43.1	- 250
5463	120.6	- 699
5340	221.9	-1286
5224	207.9	-1205
5126	0	0
5036	348.9	+2022
4950	560	+3245
4861	1001	+5801
4793	1428	+8200

fact that the rotations and the dispersion of the latter are in general much greater and are represented by quite another curve, with a minimum (maximum) at about 5000 Å. and a maximum (minimum) at 4430 Å., no wave-lengths of zero-rotation having been found in that case: the *tricyclopentanediamine-cobaltic* salt, corresponding to the *least soluble halogeno-d-tartrates*, for instance, there proved to be *levogyrotory* for all wave-lengths greater than 4000 Å.U.¹⁾.

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Physical Chemistry of the University.*

¹⁾ Cf. F. M. JAEGER, these Proceed., 40, 3, 108 (1937).

Physics. — *La courbe des densités et le diamètre rectiligne du krypton.*
Par E. MATHIAS, C. A. CROMMELIN et J. J. MEIUIZEN. Extrait
de la communication N^o. 248b du laboratoire Kamerlingh Onnes.
(Communicated by Prof. W. H. KEESOM.)

(Communicated at the meeting of February 27, 1937).

Les densités du liquide et de la vapeur saturés ont été mesurées à une série de treize températures. On a calculé les ordonnées $y = \frac{1}{2} (\delta_1 + \delta_2)$ du diamètre et on a trouvé que le krypton aussi obéit sensiblement à la loi du diamètre rectiligne.

L'équation du diamètre rectiligne est:

$$y = 1,6156 - 0,003377 T,$$

T étant la température en degrés Kelvin, conformément à l'échelle „1936”.

Le coefficient angulaire du diamètre est donc

$$\alpha = -0,003377.$$

A la température critique 209,39° K le diamètre rectiligne donne pour la densité critique

$$\Delta = 0,9085.$$

Le coefficient critique est $K = 3,443$.

Mathematics. — *Ueber Produkte von WHITTAKERSchen Funktionen.*
(Zweite Mitteilung)²⁵⁾. Von C. S. MEIJER. (Communicated by
Prof. J. G. VAN DER CORPUT).

(Communicated at the meeting of February 27, 1937).

§ 3. Integraldarstellungen für Produkte von parabolischen Zylinderfunktionen.

Aus der Definition (4) der parabolischen Zylinderfunktion geht hervor

$$\left. \begin{aligned} & D_n(z e^{\frac{1}{2}\pi i}) + D_n(z e^{-\frac{1}{2}\pi i}) \\ &= 2^{\frac{1}{2}n+\frac{1}{4}} z^{-\frac{1}{2}} \left\{ e^{-\frac{1}{2}\pi i} W_{\frac{1}{2}n+\frac{1}{2},-\frac{1}{2}}\left(\frac{1}{2}z^2 e^{\pi i}\right) + e^{\frac{1}{2}\pi i} W_{\frac{1}{2}n+\frac{1}{2},-\frac{1}{2}}\left(\frac{1}{2}z^2 e^{-\pi i}\right) \right\} \\ &= \frac{2^{\frac{1}{2}n+\frac{5}{4}} z^{-\frac{1}{2}} \pi}{\Gamma\left(\frac{1}{2}-\frac{1}{2}n\right)} M_{-\frac{1}{2}n-\frac{1}{2},-\frac{1}{2}}^*\left(\frac{1}{2}z^2\right), \end{aligned} \right\} \quad (28)$$

²⁵⁾ Erste Mitteilung: Proc. Royal Acad. Amsterdam, 40, S. 133—141 (1937).