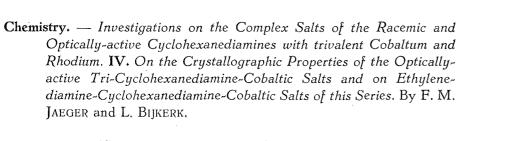
no other symmetry-elements than a hexagonal screw-axis: on the oscillationspectrograms only the basal reflections (0006) and (000.12) appear to be

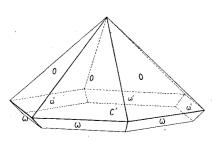


## (Communicated at the meeting of March 20, 1937).

§ 1. In continuation of our study <sup>1</sup>) on the optically active *tri-cyclo-hexanediamine-cobaltic* salts, in this paper we once more wish to draw attention to some remarkable differences of the properties of the corresponding *cyclopentane-* and *cyclohexanediamine-cobaltic* salts produced under comparable circumstances.

In the first place, these differences reveal themselves with respect to the crystalforms of these two classes of complex salts. A direct comparison of the crystalforms of the *chlorides*  $(+4H_2O)$  of both series can make this clear.

Whilst the tricyclopentanediamine-cobaltic-chloride  $+ 3H_2O$  is hexagonal, but never shows a hemimorphic development, and the salt  $+ 4H_2O$ 



is cubic-pentagone-icositetrahedral, the tri-l-cyclohexanediamine-cobaltic chloride  $+ 4H_2O$  crystallizes in the hexagonalpyramidal class, with a: c = 1: 2,730. It forms lustrous, reddish-orange crystals of typically hemimorphic habitus, (Fig. 1), with the faces:  $c' = \{000\overline{1}\}$ , very lustrous, predominant and yielding excellent reflections;  $o = \{10\overline{1}3\}$ , well developed, giving better reflections than  $\omega = \{10\overline{1}\overline{3}\}$ , which is much narrower. The symmetry here indicated was corroborated by means

Fig. 1. The Crystalform of  $D_{c} \{ Co(l-Chxn)_3 \} Cl_3 + 4 H_2O. \}$ 

of X-ray-spectrograms: the very sharp LAUE-patterns, obtained by rays parallel to the c-axis, only possess a single hexagonal axis, but no planes of symmetry (Fig. 2). From oscillation-spectrograms, the dimensions of the elementary cell were determined to be  $a_0 = 12,2$  Å. and  $c_0 = 33,3$  Å. The fundamental grating is the simple hexagonal one; the structure has

1) F. M. JAEGER and L. BIJKERK, these Proceedings, 40, 116, 246 (1937).

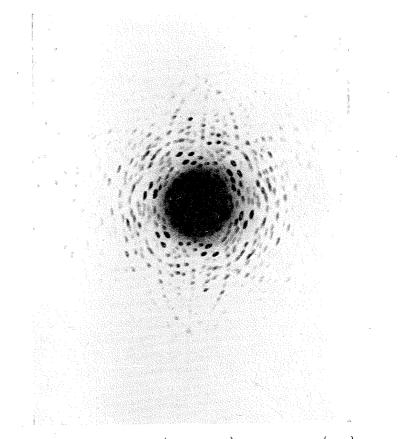


Fig. 2. LAUE-diagram of  $\{Co(l-Chxn)_3\}$   $Cl_3 + 4H_2O$  on  $\{0001\}$ .

present. The very large cell contains 6 molecules of the salt; the spacegroup is either  $C_4^2$  or  $C_6^3$ .

8		,
Angular Values:	Observed:	Calculated:
$o: o = (10\overline{1}3): (01\overline{1}3) =$	*42° 28′	
$o: o = (01\overline{1}3): (0\overline{1}13) =$	92 4 <b>3</b>	92° 50′
$o: \omega = (10\overline{1}3): (10\overline{1}\overline{3}) =$	87 17	87 10
$c: \omega = (000\overline{1}): (10\overline{1}\overline{3}) =$	46 $26\frac{1}{2}$	46 25

The crystals are completely isomorphous with those of the corresponding *rhodium* salt previously described <sup>1</sup>). They are optically uniaxial, negative and show a dextrorotation of the plane of polarisation. The specific weight is: 1.356 at  $18^{\circ}$  C.

Analysis of these crystals yielded: 14,42-14,51 % N;  $12,38 \% H_2O$ ; calculated for a salt with  $4H_2O$ : 14,51 % N and  $12,42 \% H_2O$ . The cor-

1) F. M. JAEGER and L. BIJKERK, these Proceedings, 40, 116 (1937).

responding salt, obtained by the fission of  $\{Co(r-Chxn)_3\}Cl_3 + 1H_2O$  by means of the *chloro-d-tartrates*, had exactly the same crystalform, but proved to contain only  $3H_2O$ : 9,74 %  $H_2O$  and 14,58 % N; calculated: 9,62 %  $H_2O$  and 14,96 % N. The angle: (0001) : (1013) of the *apparently bi*pyramidal crystals (by twinning), was about  $46^{\circ}22' \pm 0^{\circ}5$ .

§ 2. The optically active *chlorides* are appreciably more soluble than the inactive one, the corresponding *nitrates, chlorates, perchlorates* and *iodides* hardly more than the analogous inactive salts. Several of them were prepared from the *chloride* by means of the appropriate *silver* salts or, in the case of the iodide, by precipitation with *NaI*.

The optically active *iodide* with 3 mol. of the *l*-base and crystallizing with 2 molecules of water is much more soluble in boiling than in cold water and crystallizes from the hot aqueous solution on cooling in cubic, doubtlessly *pentagone-icositetrahedral*, small, optically isotropous crystals of a blood-red or an orange-red colour. They usually are limited by the octahedron  $\{1\overline{1}1\}$ , the corners of which are sometimes truncated by small faces of the cube  $\{100\}$ . The crystals show circular polarisation (dextrogyratory), as Dr. TERPSTRA was able to state, but they are *not* piezo-electrical. These facts also are in agreement with their pentagone-icositetrahedral symmetry.

The dextrogyratory salt: D-{ $Co(l-Chxn)_3$ }( $NO_3$ )<sub>3</sub> +  $3H_2O$  forms small, highly lustrous and orange-coloured crystals. Very beautifully developed, but very small crystals of the nitrate are deposited from a hot solution in dilute nitric acid. Their analysis proved the presence of 3 mol. of water: 7,46%  $H_2O$ ; 19,68% N; calculated for a salt with  $3H_2O$ : 8,4%  $H_2O$  and 19,66% N. They show the combination of a hexagonal prism with either an apparent hexagonal bipyramid or with two rhombohedra of opposite signs. Perhaps they are trigonal-trapezohedral, like quartz. The axial ratio (hexagonal axes) is: a: c = 1:0,7752.

Forms observed:  $m = \{10\overline{1}0\}$  and  $p = \{10\overline{1}1\}$  (or a combination of a + and — rhombohedron), both excellently reflecting. By means of the theodolite-goniometer, the angular values:

Observed:	Calculated :
$m: m = (10\overline{1}0): (01\overline{1}0) = *60^{\circ}$	
$m: p = (10\overline{1}0): (10\overline{1}1) = *48 \ 10'$	
$m: p = (01\overline{10}): (1\overline{101}) = 70$ 29	70° 31′

were measured, from which the axial ratio was calculated.

The exceptionally close analogy between these dextrogyratory crystals and those of the inactive compounds formerly described 1) also reveals itself in the external aspect, although the latter is only produced by a twinning parallel to {0001}. § 3. The salt  $\left\{ Co \frac{(Ene)_2}{(d-Chxn)} \right\} Cl_3 + 1H_2O$  was prepared either from  $(Ene)_2$ 

$$\begin{cases} C_0 \begin{pmatrix} Lnl_2 \\ P \end{pmatrix} \\ C_l \begin{pmatrix} SO_4 \end{pmatrix}_3 + \frac{1}{2} H_2 O \text{ or from } \begin{cases} C_0 \begin{pmatrix} Ene \\ Cl_2 \end{pmatrix} \\ Cl \end{pmatrix} \\ Cl \end{pmatrix}$$
 by boiling it with

I equivalent of *d-cyclohexanediamine* in absolute alcoholic solution; gradually small quantities of water are added during the heating, but an excess of the base must be avoided, because in that case simultaneously some  $Co \frac{(Ene)}{(d-Chxn)_2} Cl_3$  appears to be formed. Subsequently the solution is

( $(a^2Cnxn)_2$ ) evaporated on the water-bath, the residue dissolved in as little warm water as possible, and the solution obtained left at room-temperature for crystallization. Soon thin parallelogram-shaped tables or occasionally thicker ones are deposited, which contain 3,29 %  $H_2O$  (calculated for the salt with  $1H_2O: 4,3$  %), whilst the waterfree substance contains 20,85 % N, whilst 21,05 % N being the theoretically expected value.

The salt obtained is *rhombic-bisphenoidal*, with the axial ratio: a. b:c = 0.663:1:0.867 and the forms:  $m = \{110\}$ , broad and very lustrous;  $c = \{001\}$ , predominant, yielding sharp, but often multiple reflections;  $o = \{111\}$ , well developed, lustrous, also giving multiple images;  $\omega = \{\overline{111}\}$ , only rarely present in the thinner plates and very narrow, but well measurable. The habitus is flattened parallel to  $\{001\}$  (Fig. 3).

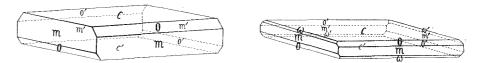


Fig. 3 Crystalform of 
$$Co \begin{pmatrix} (Ene)_2 \\ (d-Chxn) \end{pmatrix}$$
 Cl<sub>3</sub> + 1 H<sub>2</sub>O.

Angular Values:	Observed:	Calculated:
$m: m = (110): (1\overline{10}) =$	*67° 4′	
c:o = (001): (111) =	*57 30	
m:o = (110): (111) =	32 30	32° 30′
$m:o = (\overline{110}(:(111)))$	71 1	70 49

Perhaps an imperfect cleavability occurs parallel to {001}.

Optically biaxial; the plane of the optical axes is  $\{010\}$ , with the *c*-axis as first bissectrix and an apparently rather large optical angle.

The rotatory dispersion of this salt was measured; the data obtained are collected in Table I.

The molecular rotations are greater than those of the *tri-d-cyclohexanediamine* salt, but the curve of the rotatory dispersion has a similar shape.

<sup>&</sup>lt;sup>p</sup>) F. M. JAEGER and L. BIJKERK, these Proceedings, **40**, 116, 246 (1937).

TABLE I. Rotatory Dispersion of $C_{O} \xrightarrow{(Ene)_2}_{(d-Chxn)} Cl_3 + 1 H_2O$			
Wavelength λ in A.U. :	Specific Rotation [a]:	Molecular Rotation [M]. 10 <sup>-2</sup> :	
6980	— 37°	— 154°	
6730	- 34	- 142	
6480	- 31	- 129	
6262	- 26.5	- 110	
6074	- 12	- 50	
5893	+ 19.5	+ 80	
5753	+ 77	+ 320	
5592	-+ 170	+ 708	
5463	+ 320	+1333	
5340	+ 460	+1917	
5224	+ 500 M	+2083 M	
5126	+ 470	+1958	
5036	+ 190	+ 792	
4950	— 290	-1208	
4861	760	- 3165	
4793	—1490 m		
4724		5000	
4658	-1110	—4625	
4596	1080	4500	
4537			
4483	- 910		

§ 4. In the mother-liquor just described a crop of prismatic crystals was found, which proved to consist of the salt:  $\begin{cases} Co & (Ene) \\ (d-Chxn)_2 \end{cases} Cl_3 + 3\frac{1}{2}H_2O$ . The analysis yielded a not quite constant watercontent of 11,8—12,2%  $H_2O$  (theoretically, for  $4H_2O$ : 13,7%) and 16,13—16,55% N (theoretically: 16,26% N); the anhydrous salt gave: 23,31% Cl, calculated: 23,48% Cl.

By boiling an aqueous solution of  $\left\{ Co \frac{(d-Chxn)_2}{Cl_2} \right\} Cl$  with 1 equivalent

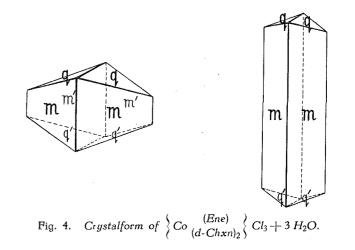
of *ethylenediamine*, no good results were obtained, because under these conditions evidently a fission of the product formed into the *tricyclohexane-diamine-* and the *triethylenediamine* salts occurs.

Better results were obtained when the experiment was repeated by adding *two* equivalents of the base to the *praseo-salt*. In this case a yield of the desired salt was obtained amounting to about half the expected quantity, and about the same yield of the *diethylenediamine-cyclohexanediamine-compound*. The two salts can be separated by fractional crystallizations and identified by their individual crystalforms, because first.

 $\left\{ \begin{array}{c} Co (Ene) \\ (d-Chxn)_2 \end{array} \right\} Cl_3$  is deposited from the solution and subsequently the other salt.

The salt  $\left\langle Co \frac{(Ene)}{(d-Chxn)_2} \right\rangle Cl_3 + 3\frac{1}{2}H_2O$  crystallizes in *rhombic* needles or

thicker crystals; most probably they have *rhombic-bisphenoidal* symmetry, although this could neither be corroborated by piezo-electrical phenomena, nor by the study of the habitus of the crystals (Fig. 4).



The crystals are either apparently octahedrally shaped individuals or long needles; in both cases only the forms  $m = \{110\}$  and  $q = \{011\}$  are present; the faces of both forms are highly lustrous and the crystals show very constant angular values.

Angular Values:Observed:Calculated: $m: m = (110): (1\overline{10}) = *70^{\circ} 4'$ - $q: q = (011): (0\overline{11}) = *42$ 7m: q = (110): (011) = 787 $78^{\circ} 5\frac{3}{4}'$ 

No distinct cleavability was observed.

Optically biaxial; the plane of the optical axes is probably {100}.

The rotatory dispersion of this salt was measured in a 0,1 % solution; the data obtained are collected in the following table:

	Dispersion of $Co_{(d-Chxn)}^{(Ene)}$	
Wavelength $\lambda$ in A.U.:	Specific Rotation [ a]:	Molecular Rotation [M]. 10 <sup>-2</sup> :
6980	— 55°	- 284°
6730	- 53	— 274
6480	50	— <b>2</b> 58
6262	50	- 258
6074	- 50	- 258
589 <b>3</b>	20	— 10 <b>3</b>
5753	+ 20	+ 103
5592	+ 120	+ 620
5 <b>4</b> 63	+ 230	+1189
5340	+ 350	-+1809
52 <b>24</b>	+ 390 M	+2015 M
5126	+ 259	+1340
5036	+ 30	+ 155
4950	670	3462
4861	_1026	5300
4793	—1560 m	—8060 m
4724	1480	_7646
4658	1370	7080
4596		6665
4537	_1180	6097
4483	1100	

These data, together with those of the previous salt, have already been graphically represented in Fig. 8 of our former paper 1) and the curves obtained have been compared with that of L-{Co(d- $Chxn)_3$ } $Cl_3$ , as well as with that of D-{ $Co(Ene)_3$ } $Cl_3$ . The analogies of the four curves at once become evident from this figure, as well as the shifts of the different zero-

points of the *L*-salts on gradually introducing more molecules of *d*-cyclohexanediamine into the complex ions, instead of the molecules of ethylenediamine in the triethylenediamine-ion: evidently there is present an almost pure superposition of the levogyratory influence of the *d*-diamine molecules introduced upon the rotation of the resolved complex ion itself, so that the rotation in the red part of the spectrum becomes negative, although the character of the dispersion of the D-{ $Co(Ene)_3$ }<sup>...</sup>-ion has actually been preserved.

§ 5. By the interaction of 1 molecule of *ethylenediamine* and 1 molecule of the praseo-salt:  $\left\{ Co \begin{pmatrix} (r-Chxn)_2 \\ Cl_2 \end{pmatrix} \right\} Cl$ , in the same way one can try to prepare the corresponding *dicyclohexanediamine-ethylenediamine-cobaltic chloride*:  $\left\{ Co \begin{pmatrix} (r-Chxn)_2 \\ (Ene) \end{pmatrix} \right\} Cl_3$ . The *chloride* obtained is very soluble, but crystallizes from its hot, saturated solutions, in the form of fine, lustrous, brown-red needles which, however, proved to be  $\{Co(r-Chxn)_3\}Cl_3$ . Evidently, therefore, the racemic salt cannot be prepared in this way.

In the same way the corresponding diethylenediamine-r-cyclohexanediamine-cobaltic salt was prepared from the red diethylenediamine-chloroaquo-cobaltic sulphate  $(+1,5H_2O)$  by dissolving 32 grammes of the latter in 150 cm<sup>3</sup> water and, after the addition of 12 grammes of r-cyclohexanediamine, by boiling the solution at a reflux-cooler during several hours. On evaporation of the reddish-brown solution to a small volume on the waterbath, a chocolate-brown, very soluble salt is obtained, which is dissolved into a small quantity of cold water and, after heating the solution with norite, is precipitated in the form of the orange coloured iodide by an excess of NaI. The orange precipitate is filtered off, washed with water and alcohol, dissolved in as little boiling water as possible, the solution filtered off from a small quantity of cobaltous oxide and left for crystallization.

The *Nal*-solution still contains some of the impure iodide, which can be obtained from it and purified in the same way; the total yield of the salt obtained is practically the theoretical one.

The *iodide* crystallizes either in the shape of fine, red-orange coloured needles or in octahedrally shaped, small, rhombic crystals, which contain 1-1.5 mol. water of crystallization. The salt can in the same way also be

prepared from the praseo-salt:  $Co \begin{pmatrix} Ene \\ Cl_2 \end{pmatrix} Cl.$ Analysis: 54,95 % I; 8,52 % Co; 12,13 % N and about 3,7 %  $H_2O$ ;

Analysis: 54,95 % I; 8,52 % Co; 12,13 % N and about 3,7 %  $H_2O$ ; calculated for  $\begin{cases} Co (Ene)_2 \\ (r-Chxn) \end{cases} I_3 + 1H_2O$ : 55,06 % I; 8,53 % Co; 12,14 % N and 2,60 %  $H_2O$ .

The crystals are *rhombic-bipyramidal* (Fig. 5), with the axial ratio: a:b:c=0.85:1:1.66.

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<sup>&</sup>lt;sup>1</sup>) F. M. JAEGER and L. BIJKERK, these Proceedings, 40, 257 (1937).

Often the limiting planes are curved, but from oscillations-spectrograms

round the three axes the dimensions of the primary cell were found to be:

$$a_0 = 11.4 \text{ Å}; b_0 = 13.4 \text{ Å}; c_0 = 22.3 \text{ Å}.$$

from which the axial ratio just mentioned can be deduced.

Angular Values:

o: o = (111): (111) = 74° 12
$$\frac{1}{2}'$$
  
o: o = (111): (11 $\overline{1}$ ) = 42 37 $\frac{1}{2}$   
o: o = (111): ( $\overline{1}$ 11) = 90 26

Sometimes the crystals have an apparently hemimorphic shape, but evidently they are holohedral. The crystalform, although analogous to that of the corresponding *triethylene-cobaltic iodide*  $(+1H_2O)$ , certainly is different from the latter <sup>1</sup>).

 $\begin{cases} Co & (Eine_2) \\ (r-Chxn) & I_3 + 1 H_2O. \end{cases}$ § 6. Experiments were also made with the purpose of resolving the salts derived from the racemic base into their optically active anti-

podes by means of the *chloro-d-tartrates*. In the case of  $Co \frac{(Ene)}{(r-Chxn)_2} Cl_3$  it could be proved that also under the prevailing conditions this salt is rather unstable, exactly as was previously mentioned.

From the least-soluble *chloro-d-tartrate* a *chloride* was obtained, which proved to be *ditetragonal*, showing  $m = \{110\}$  predominant and  $o = \{111\}$ ; taking  $m = \{100\}$  and  $o = \{101\}$ , these crystals prove to be identical with those of the *racemic* salt:  $\{Co(r-Chxn)_3\}Cl_3+1H_2O$ , with: a:c=1:0,7212; they are optically uniaxial, negative. Evidently the original salt is, owing to the action of the solvent, primarily transformed into a mixture of  $\{Co(r-Chxn)_3\}Cl_3+1H_2O$  and  $\{Co(Ene)_3\}Cl_3+3H_2O$ ; then the two salts, by the action of the *Ag-d-tartrate*, are partially resolved into the least-soluble *chloro-d-tartrates*, from which, indeed, another chloride could be isolated, the rotation of which was identical with that of L- $\{Co(d-Chxn)_3\}Cl_3+3H_2O$ . There is every reason, therefore, to suppose that the salt  $\{Co (r-Chxn)_2\}Cl_3$  is, under all circumstances, really rather unstable when in contact with its solution, and that it is decomposed in the way indicated above.

As to the fission-experiments of the salts of the formula:  $\begin{cases} Co \frac{(r-Chxn)}{(Ene)_2} \end{cases} X_3, \end{cases}$ 

the following remarks can be made. The fission was tried in the case of the bromide  $(+1H_2O)$  by means of the bromo-d-tartrates in the usual way.

But in this case no positive results could be obtained either: the difference in the solubilities of the two highly soluble *chloro-* or *bromo-d-tartrates* evidently is too small to allow a fission. Moreover, a treatment of the salt with the hot mother-liquors, with solutions of the *Ag-tartrate*, etc., very rapidly causes it to be decomposed into the *tricyclohexane-* and *triethylenediamine* salts, so that finally these tentatives were stopped.

§ 7. Finally we tried to ascertain also in the case of the optically active cyclohexanediamines, in how far these molecules possibly could be introduced into complex ions of this kind, in which optically active molecules are already present. For this purpose we chose the praseo-salt:  $\begin{cases} Co \begin{pmatrix} (l-Cptn)_2 \\ Cl_2 \end{pmatrix} \\ Cl \end{pmatrix} \\ Cl and, by heating it alternately with d- or l-cyclohexane-diamine in the theoretical quantity, we tried to produce the compounds: <math>\begin{cases} Co \begin{pmatrix} (l-Cptn)_2 \\ (d-Chxn) \end{pmatrix} \\ Cl_3 \end{pmatrix} \\ Cl_3 and \\ Co \begin{pmatrix} (l-Cptn)_2 \\ (l-Chxn) \end{pmatrix} \\ Cl_3 respectively. A detailed study of the compounds thus obtained has taught us, however, that beyond all doubt the products mentioned are not stable, neither in the case where three levogyratory molecules are present in the ion, nor in that of the simultaneous presence of two levo- and one dextrogyratory molecule. The products isolated always were: <math>\{Co(l-Cptn)_3\}Cl_3$ , besides  $\{Co(d-Chxn)_3\}Cl_3$  or  $\{Co(l-Chxn)_3\}Cl_3$  respectively. Neither proves it possible to prepare

the compound  $\left\{ Co \frac{(l-Chxn)_2}{(d-Chxn)} \right\} Cl_3$ ; etc.

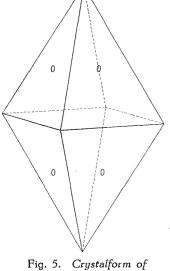
The decomposition of the primarily formed salts by the contact with the solute evidently takes place in exactly the same way as was observed by us in all analogous cases, namely according to the reaction-scheme:

 $3 \left\{ Me \begin{array}{c} X_2 \\ Y \end{array} \right\} Cl_3 \rightarrow 2 \{ Me X_3 \} Cl_3 + \{ Me Y_3 \} Cl_3. \text{ This fact thus once more} \right\}$ 

confirms the strong tendency of such complex ions to assume the possibly highest symmetrical configurations of identical substitutes round their central atom.

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

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<sup>&</sup>lt;sup>1</sup>) F. M. JAEGER, Recueil d. Trav. d. Chim. d. Pays-Bas, 38, 205 (1919). The axial ratio of the *triethylenediamine* salt is a:b:c=0.87:1:1.74.