**Chemistry.** — *On the spatial Arrangement and Rotatory Dispersion of optically active Complex Salts of Cobalt and Rhodium.* By Prof. Dr. F. M. JAEGER and Dr. H. B. BLUMENDAL.

§ 1. In the following pages some investigations are shortly reviewed, which were recently made in this laboratory with the purpose to answer the question: what changes in the rotatory dispersion of optically active complex salts of the *Triethylenediamine-Cobaltic*-type will be caused by gradually substituting the three molecules *ethylenediamine* in the complex ion by one, two or three molecules of another optically-active bivalent base, possessing itself, like *ethylenediamine*, a certain degree of axial symmetry? And furthermore: what will be the number of isomerides in these cases, and what will be their spatial arrangement, in connection with that of the active molecules introduced?

It may be remarked that already in the simplest case, i.e. that, in which all three *ethylenediamine*-molecules of the complex Co-, or Rho-cations are replaced by three molecules of an optically-active base, — the reaction may lead to a rather considerable number of isomers, if the *racemic* base, acting as *d,l*-base, be used in it. For, if the dextro- and levo-rotatory components be indicated by *d* and *l*, the racemate by $r (= d,l)$, but the dextro-, respectively levorotatory configurations of the complex ion by *D* and *L*, — then the action of 3 molecules of the racemic base, being such that only an *odd* number of optically-active molecules can be used for the formation of each cation, can lead already, theoretically, to the following *eight* combinations:

$$[ddd]_D \; ; \; [lll]_D \quad ; \; [ddl]_D \; ; \; [dll]_D \; ;$$
$$[ddd]_L \; ; \; [lll]_L \; ; \; ; \; [ddl]_L \; ; \; [dll]_L \; ;$$
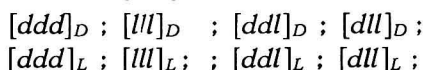
if no special causes be indicated beforehand, why one of these configurations should be impossible. As, moreover, these 8 cases represent in pairs each other's mirror-images, e.g.: $[ddl]_D$ and $[dll]_L$; etc., — the said derivatives may be in pairs combined in aequimolecular quantities, yielding in this way 4 *racemates* and 24 *partial racemates*.

It is worth while remarking here, that all such cations, in which 3 *identical* molecules are present, — as is the case also in the *triethylenediamine*-complexes mentioned already, — will possess the rather high degree of symmetry D_3, this being the symmetry of *d*- and *l-quarz*, if only the substituents themselves have a single binary axis of symmetry. But in other cases, as e.g.: $[ddl]$; etc., this degree of symmetry of the cation must be much less, even if the condition just mentioned be

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fulfilled. In this case the complex ions will only have a single polar binary axis (C_2). In both cases, however, these complex ions may be separated into two different mirror-images, because their symmetry is always a purely axial one.

§ 2. We have chosen as a bivalent base apparently well suited to the said purpose, the 1-2-*Diamino-cyclopentane* (=*Cyclopentylene-diamine*), — a substance unknown up till now. As may be seen from the following formulae, this compound may occur in a *cis-* and a *trans*-configuration:
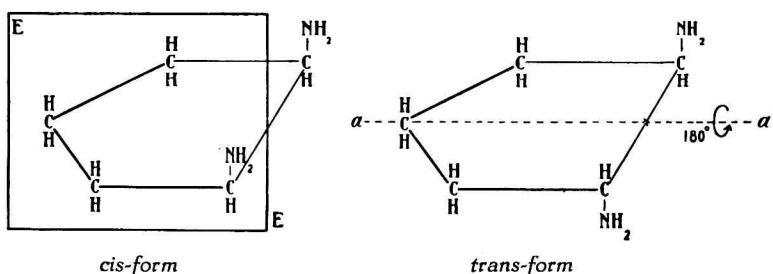
cis-form   trans-form

of which, however, the *cis*-form, having a plane of symmetry perpendicular to the plane of the carbon-cycle, is not different from its mirror-image; while the *trans*-form, which possesses only a single binary axis of symmetry, situated *in* the plane of the carbon-cycle, — may under favourable circumstances, evidently be separated into non-surperposable mirror-images.

It appeared, however, pretty soon during the preparation of the new base, in which, in principal features, the following way was followed: *Trimethylenedicyanide→Glutaric Acid→Diethyl-Glutaric Ester→Diethyl-Cyclopentanedione-dicarbonic Ester* (obtained by condensation with *oxalic ester*) → *1-2-Cyclopentanedione* → *1-2-Cyclopentanedioxime* → (by reduction with an excess of *sodium* and *alcohol*)→*1-2-Diaminocyclopentane*, — that *exclusively* the *trans*-compound was formed. Because a reduction of the *dioxime* appeared to be possible only in an alkaline medium, — it being highly sensitive to acids, — no trace of the *cis*-derivative could hitherto be obtained, not even by catalytic reduction. The *trans*-configuration of the base obtained, — which boils under atmospheric pressure at 170° C. and which yields a beautifully crystallized *diacetyl*-derivative (mpt.: 219° C.), — was proved exactly by the possibility of separating it into two optical antipodes by means of *d-* and *l-tartaric acids*.

If, for instance, the racemic base be converted into its *bi-d-tartrate*, the *bitartrate* (mpt. 143°—144° C.) of the *levo*rotatory base first crystallizes; etc. The boilingpoint (1 atm.) of this base is 166° C. The specific rotations of the pure optically-active base are: for red: — 38°, for violet: — 113°,5.

We have also made a number of trials to convert the *trans*-base into

an *oxalyl*-derivative, either by means of *diethyloxalate*, or by means of *oxalylchloride*, and to separate from it the *cis*-derivative. But no positive results were obtained in this way: the *trans*-configuration seems to be so extremely stable in comparison with the *cis*-form, that this last appears to be re-arranged immediately into the first one. For this reason we will speak in the following page only of the *d*-, the *l*-. and the *rac. trans-1-2-Diaminocyclopentane*.

§ 3. Circumstances appear to be simplest, if we draw our attention in the first place to the complex *Rhodium*-salts, which are obtained in the reaction between *racemic trans-1-2-Diaminocyclopentane* and crystalline *sodium-rhodiumhexachloride* (hydrated, powdered). Subsequently the same reaction can be executed with each of both antipodes of the base; the products thus obtained serving to be immediately compared with the former ones.

In treating the solid $Na_3 Rho Cl_6$, 9 aq. with the *racemic* base, besides a small quantity of an orange-coloured by-product, soluble in alcohol [1]), only a single white, crystalline product was obtained, which, by means of *NaJ*, could readily be precipitated as a colourless *iodide*, from which a whole series of other salts could be prepared by means of *silver*salts such as $AgCl$, $AgBr$, etc. The *iodide* had the composition: $\{Rho (Cptdine)_3\} I_3 + 1 H_2O$; the corresponding *chloride* crystallizes with $2 H_2O$.

By converting this *chloride* by means of *Ag-d-tartrate*, respectively *Ag-l-tartrate*, into the corresponding *chloro-d-*, resp. *chloro-l-tartrates*, it could be proved that the original salt is a true *racemic* compound, from which two optically-active antipodes could be separated. If *Ag-d-tartrate* was used, the less soluble fraction of the *chloro-d-tartrates* thus obtained, gave a *chloride*, which in solution appeared to be strongly *levorotatory*. By careful fractional crystallisation and by determining the complete curve of rotatory dispersion of these fractions, it could be proved with certainty, that no other components than the dextro-, respectively levorotatory salts mentioned, were present in the original reaction-product.

If now only the *d*-, or the *l*-base were used in the same reaction, then in each case only a *single* optically-active product appeared to be generated. By accurate measurement of the rotatory dispersion of both these salts and by comparing them with the products obtained by the fission of the racemic compound mentioned above, it could be proved

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[1]) The orange-coloured by-product, treated with *NaJ*, gave an intensely orange-coloured *iodide*, which, on heating its alcoholic solution, was gradually decomposed under precipitation of the ordinary white *iodide*, mentioned above. By analysis we were able to prove that most probably a double compound is present here, consisting of 2 mol. of the white *iodide* and 1 mol. of a non-ionogenic complex, containing *Rho, Cl*, alcohol and *Diaminocyclopentane*.

with complete certainty, that in the *levo*rotatory complex cation only *three* molecules of the *d*-base, in the *dextro*rotatory complex cation only *three* molecules of the *l*-base were p.esent. *No other salts than those of the* ions: $\{Rho(lll)\}_D^{..}$ and $\{Rho(ddd)\}_L^{..}$ were generated in the reaction between the *racemic Diaminocyclopentane* and $Na_3 Rho Cl_6$, 9 aq.

The complete curve of the rotatory dispersion of these salts is represented in Fig. 1.
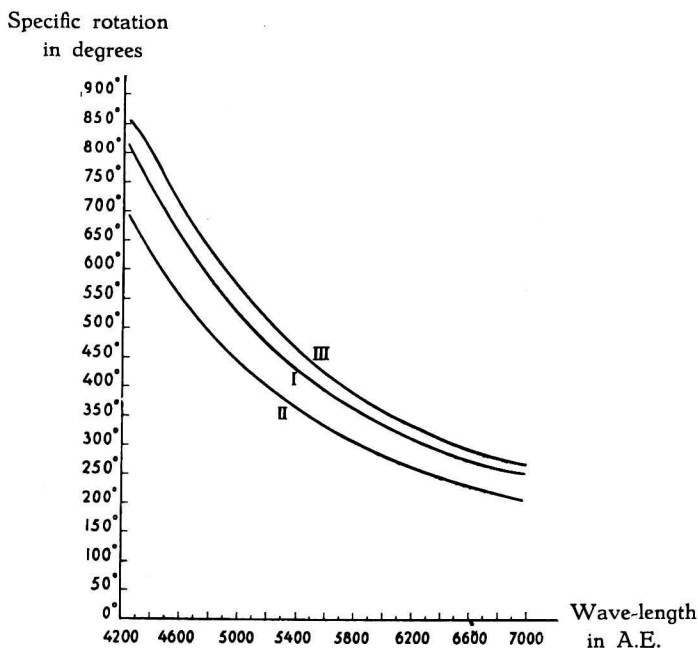

Fig. 1.

Rotatory dispersion of $\{Rho\,(l\text{-}Cptdine)_3\}\,Cl_3$ and its *d*- and *l*-Chloro-tartrates

From this it must be concluded, that the *levo*rotatory configuration of the complex ion is incompatible with the presence of 3 *levo*rotatory molecules of the base in it; and that, in the same way the presence of 3 *dextro*rotatory molecules of the base is incompatible with the *dextro*rotatory configuration of the complex *Rho*-ion.

In the case of the racemic *perchlorate*, which forms anhydrous crystals, a fission into the antipodes was observed by *spontaneous crystallisation* of the solutions at roomtemperature. The crystals deposited were octahedral, and, if selected and individually solved, they gave solutions, which were dextro-, or levorotatory. The determination of the solubilities of the racemic compound and of the antipodes taught us, that a case of spontaneous crystallisation was present here with a *minimum* transformation-temperature of 48° C. for the racemoid, the racemic compound becoming the stabler phase above this temperature (Fig. 2). The said transformation may be represented by:

d-[{Rho ($Cptdine$)$_3$} (ClO_4)$_3$ + 12 H_2O] +
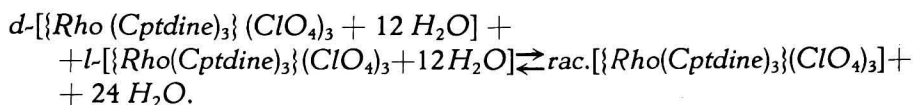
    +l-[{Rho($Cptdine$)$_3$}(ClO_4)$_3$+12H_2O]$\rightleftarrows$$rac$.[{$Rho$($Cptdine$)$_3$}($ClO_4$)$_3$]+

    + 24 H_2O.

The fission of the anhydrous racemic compound, in presence of the solution, into the highly hydrated antipodes must, therefore, evidently occur under an evolution of heat.

Solubility in grammes
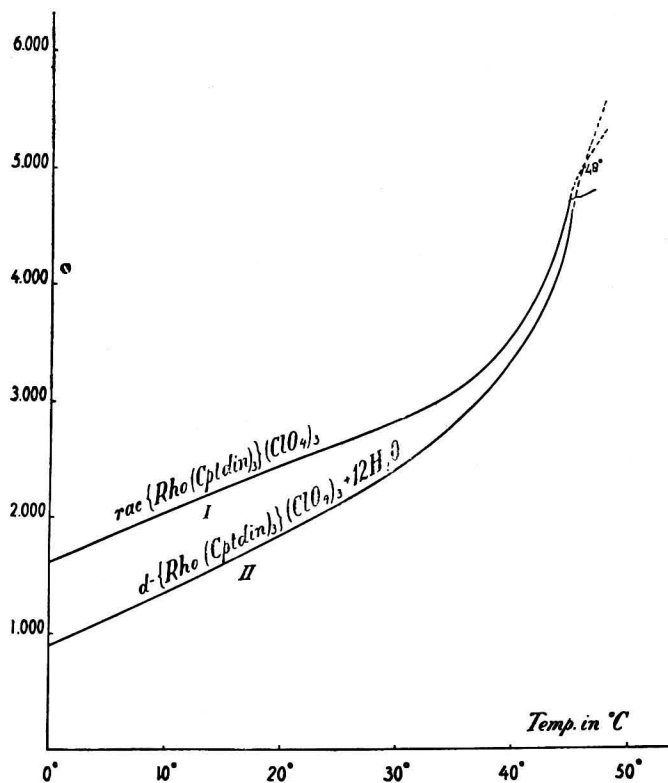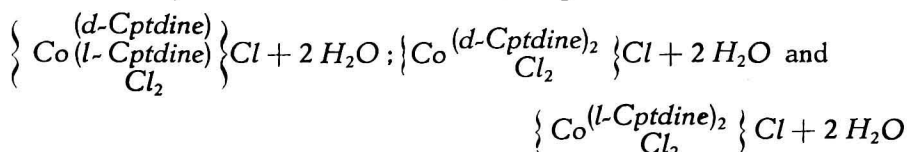anhydrous salt in 100 cm³ sol.

Fig. 2.

Solubility of rac. and dextro-rot. { Rho ($Cptdine$)$_3$ } (ClO_4)$_3$ at different temperatures.

The optically-active *chlorides* (+ 4H_2O), *nitrates* (+ 4 H_2O), *chlorates* (+ 12 H_2O) and *perchlorates* (+ 12 H_2O) are all crystallising in beautiful *octahedral* crystals of *pentagone-icositetrahedral* symmetry. In the case of the *chlorides* and *nitrates* also hydrates with 3 H_2O were met with, which are formed in the solution at somewhat higher temperatures, and which possess a *hexagonal-bipyramidal* symmetry. Some *Roentgen*-spectroscopical investigations of the structure of these crystals will later-on be published elsewhere, which confirm these conclusions.

§ 4. The phenomena occurring in the preparation of the corresponding *cobaltic* salts, appear to be of an analogous nature. As the oxydation of a solution of $CoCl_2$ + *Diaminocyclopentane* with air gave no good

results, the formation of the cobaltic salt was performed by means of a 10 % solution of *hydrogenperoxyde*: 7.5 Gr. $CoCl_2$ in 25 cm^3 water were, in a wide flask, mixed with 5 Gr. *Diaminocyclopentane* and then 60 cm^3 of a 10 % solution of H_2O_2 were slowly added to it. When the reaction is finished, 100 cm^3 strong *HCl* are added to the solution and the liquid is then heated on the water-bath; soon the *praseo*-salt formed begins to precipitate.

The precipitate is then filtered off from the mother-liquid and so long washed with alcohol and ether, till complete neutral reaction is attained. The yield is about 6,2 Gr. of the *praseo*-salt; in the mother liquid there is still present some salt of the composition: $\{Co(Cptdine)_3\}Cl_3$, which can be obtained by precipitation as *iodide*. In subsequently using in this reaction the racemic base or one of its optical-active antipodes, it seems to be possible to obtain the following salts:

$$\left\{ Co \begin{matrix} (d\text{-}Cptdine) \\ (l\text{-}Cptdine) \\ Cl_2 \end{matrix} \right\} Cl + 2\,H_2O \; ; \left| Co \begin{matrix} (d\text{-}Cptdine)_2 \\ Cl_2 \end{matrix} \right\} Cl + 2\,H_2O \text{ and}$$

$$\left\{ Co \begin{matrix} (l\text{-}Cptdine)_2 \\ Cl_2 \end{matrix} \right\} Cl + 2\,H_2O$$

These salts give, on heating them with a third molecule of one of the three bases mentioned, the desired *Tri-diaminocyclopentane-Cobaltic*-salts.

Both the last mentioned, bluish-green *praseo*-salts are optically-active; their molecules are different from their own mirror-images, but of course, they can individually not be separated. In Fig. 3 are reproduced the curves of rotatory dispersion of these *praseo*-salts, and that of the
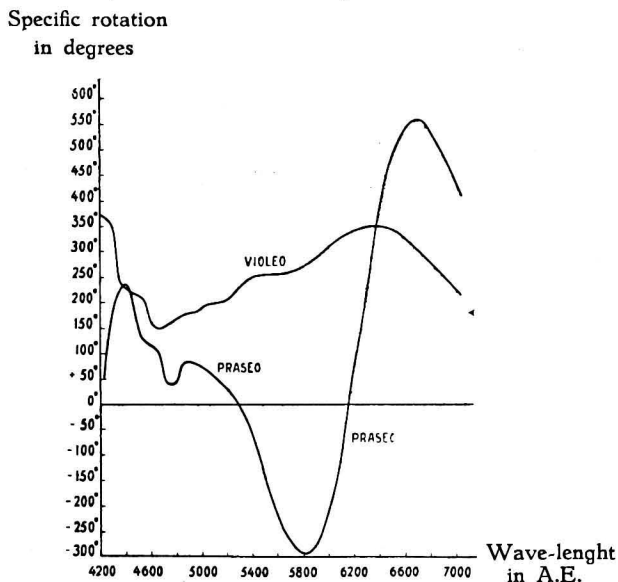

Fig. 3.

Rotatory dispersion of the *Praseo*- and *Violeo*-$\left\{ Co \begin{matrix} (l\text{-}Cptdine)_2 \\ Cl_2 \end{matrix} \right\} Cl.$

corresponding *violeo*-salts obtained by soft heating of the solutions of the first. The *praseo*-salt first mentioned above cannot be split into its antipodes, because its cation having a plane of symmetry perpendicular to the plane in which the two molecules of the base are situated. This salt, which is optically-inactive, must differ, therefore, from the true racemic compound obtained by mixing aequimolecular quantities of the second and third and by letting them crystallise from their mixed solutions. However, experience taught us, that this racemic compound could by no means be distinguished from the salt prepared from the racemic base; evidently the true racemic salt is likewise generated in this last reaction, so that the first of the three formulae mentioned above may be excluded beforehand.
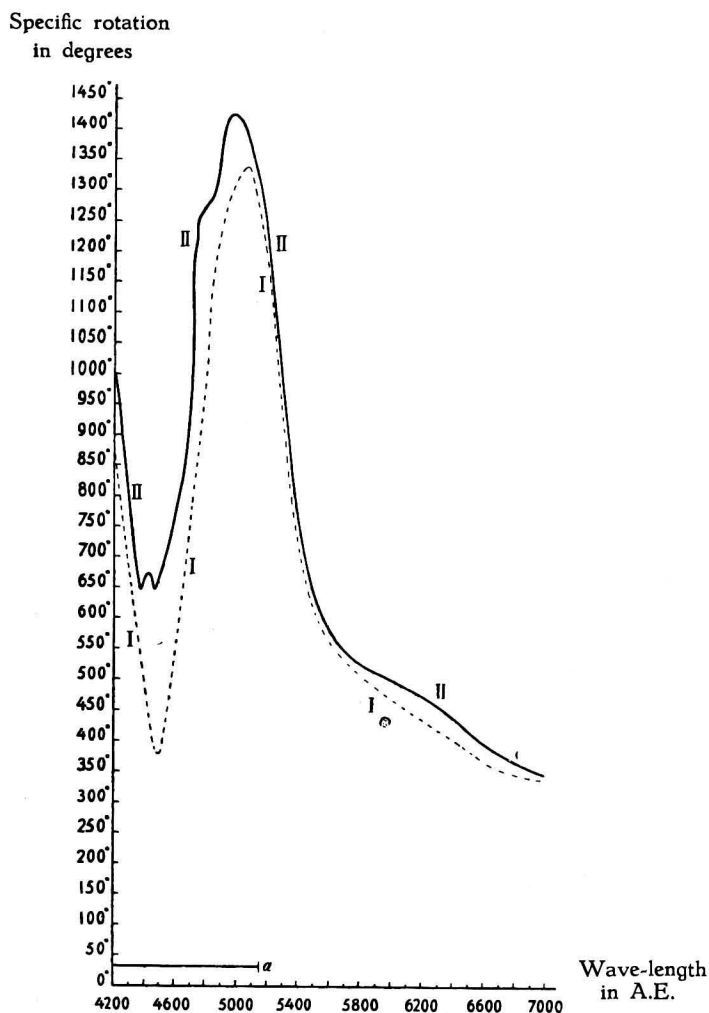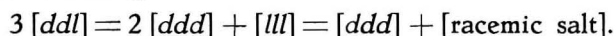

Fig. 4.

Rotatory dispersion of d-$\{$ Co $(l$-$Cptdine)_3$ $\}$ Cl_3 and its *Chloro-l-tartrate*.

By heating the *praseo*-salts with an excess of the base, we were able to obtain the corresponding *tri-diaminocyclopentane-cobaltic*-salts, as well in their racemic, as in their optically-active forms. In this case also, the racemic salt could be separated into its antipodes by means of the *chloro-d-*, and *chloro-l-tartrates*. The less soluble *chloro-d-tartrate* gave also in this case, — exactly as with the *Rho*-salts, — a *chloride*, which in solution was strongly *levo*rotatory. It could be proved, by comparing its rotatory dispersion with that of the salts prepared from the active bases, that the constitution of its cation was: $[ddd]_L$. From this it becomes evident, that the behaviour of the *Rho*- and *Co*-salts is completely analogous; simultaneously the direct proof is given here of the view since long held by one of us [1]), that the *Co*- and *Rho*-salts of the same spatial configuration show the *same* algebraic sign of their rotations, and *not*, as WERNER [2]) pointed out, opposite rotations. In the case of these *cobaltic* salts there also appeared to be formed only *two* kinds of complex cations with to active bases: $[lll]_D$ and $[ddd]_L$, all other combinations being rigorously excluded by steric causes. Therefore, there is also only *one* racemic compound.

The curve of rotatory dispersion of these salts is reproduced in Fig. 4.

If in the *praseo*-salts of the types: $\left[Co_{Cl_2}^{(d)_2}\right]X_3$, respectively $\left[Co_{Cl_2}^{(l)_2}\right]X_3$, one tries to introduce a molecule of the *l-*, respectively of the *d*-base, in the hope of obtaining the salts of the type: $\left[Co_{(l)}^{(d)_2}\right]X_3$ and $\left[Co_{(d)}^{(l)_2}\right]X_3$ respectively, — it appears, that this does not happen. The expected combinations seem to be unstable from steric causes, and only a mixture of 1 molecule of an active salt with three identical molecules of the base in its cation, besides 1 molecule of the racemic compound is obtained in each case, according to the reaction-scheme:

$$3\,[ddl] = 2\,[ddd] + [lll] = [ddd] + [\text{racemic salt}].$$

In this case also the formation of the cations with the *highest* possible symmetry is evidently favoured at the cost of the complexes of a lower degree of symmetry.

§ 5. In general the crystalforms of the racemic and optically-active *Co*- and *Rho*-salts appear to be quite analogous. The optically-active components here also crystallize in octahedral crystals of pentagone-icositetrahedral symmetry. In the case of the *chloride* and of the *nitrate*, there exist, here also, besides the cubic forms, hexagonal-bipyramidal hydrates, crystallizing with $3\,H_2O$.

Moreover, the corresponding *perchlorate* shows also in this case the

[1]) F. M. JAEGER, Proceed. Royal Acad. Amsterdam, **20**, (1917) 264, 265. Chem. Weekbl. **14**, (1917), 728; Recueil d. trav. chim. Pays-Bas, **38**, (1919), 170; *Lectures on the Principle of Symmetry*, 2nd Edit. (1920), p. 251.

[2]) A. WERNER, Ber. d. d. chem. Ges., **45**, (1912), 1229.

phenomenon of a spontaneous fission into its antipodes by crystallisation at room-temperature. This is most remarkable, because circumstances are here just the same as those in the case of the *Rho*-salts: the transformation-temperature, — if really existing, — must be here also a *minimum* temperature in the neighbourhood of $-1°.5$ C., as is clearly demonstrated by the results of the determinations of the solubilities (see Fig. 5). A direct measurement of this transition-temperature is impossible, because at those low temperatures the solubilities have become already so very small, that the actual depression of the freezing-point is too insignificant, to retain under these conditions the appearance of a liquid solution besides the solid phase; all is here already converted into a solid mixture of ice and salt.

But in every case, we must conclude that at all temperatures above
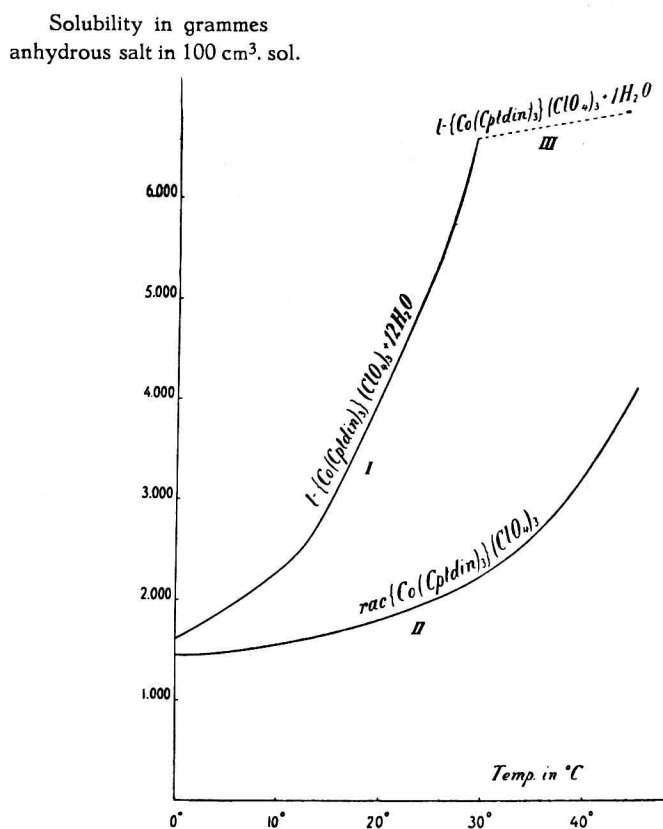

Fig. 5.

Solubility of rac. and levo-rot. $\{ Co\,(Cpt\ ine)_3 \} (ClO_4)_3$ at different temperatures.

$0°$ C., the optically-active, octahedral crystals must be *metastable* with respect to the racemic compound. Therefore, it is very remarkable that, notwithstanding this, these octahedral crystals are yet deposited in the inactive solution at room-temperature. That the components are really

metastable with respect to the racemic compound under these conditions, can be also seen from the fact, that if the saturated solutions be inoculated with a germ of the crystallized racemic salt, the octahedral crystals will gradually disappear in favour of those of the racemic compound.

Moreover, the colour of these *Co*-salts is highly remarkable: they being clear *pink*, as true *cobalto*-salts in solution, instead of having the deep orange or bloodred colour of the *triethylenediamine-cobaltic*-salts. The *iodide*, however, is an exception to this, showing the true colour of the *luteo*-series.

The specific and molecular rotations of these *Co*- and *Rho*-salts are, moreover, for the same wave-lengths many times greater than those of the corresponding *triethylenediamine*-salts: the absolute values of the specific rotations are, in the case of the *cobaltic*-salts, about 3 to 10 times, in the case of the *Rho*-salts about 7 to 8 times greater than they are in the corresponding salts of the *triethylenediamine*-series. The rotatory dispersion of the *Rho*-salts, on the other hand, does not differ in both cases to the same degree as the rotations themselves.

§ 6. Much more complicated, however, are the phenomena observed, if besides *Diaminocyclopentane*, one tries to get complex salts of *cobaltum*, whose cations do also contain 1 or 2 molecules of *ethylenediamine*.

For the preparation of salts of the type: $\left\{Co\begin{matrix}(E\ddot{\imath}ne)_2\\(Cptdine)\end{matrix}\right\}Cl_3$, we can start with the green *praseo-*, or the pink *chloro-aquo-cobaltic*-salts containing 2 molecules of *ethylenediamine* in their complex ions.

If e.g. salts like: $\left\{Co\begin{matrix}(E\ddot{\imath}ne)_2\\Cl_2\end{matrix}\right\}Br$ or $\left\{Co\begin{matrix}(E\ddot{\imath}ne)_2\\Cl\\H_2O\end{matrix}\right\}Br_2$ are treated with racemic or *d-*, and *l-Diaminocyclopentane*, there are really formed salts of the type desired. The simplest case is that, where 1 molecule of the *racemic* base is used. An optically-inactive salt, having the colour of the ordinary *triethylenediamine-cobaltic*-salts, is produced in this case, which appears to be a true racemic compound, as is proved by its possible fission into two optically-active antipodes by means of the *bromo-d-*, respectively the *bromo-l-tartrates*. In fig. 6 is reproduced the dispersion-curve (II) of the *bromide*, prepared from the less soluble *bromo-d-tartrate*; this *bromide* was proved to have the constitution: $\left\{Co\begin{matrix}(E\ddot{\imath}ne)_2\\(l\text{-}Cptdine)\end{matrix}\right\}_D Br_3 +$ $2 H_2O$. The other component gave the same rotations, but with opposite signs.

The difference in the character of this dispersion-curve with that of the salt of the ion: $\left\{Co(l\text{-}Cptdine)_3\right\}_D^{\cdots}$ is very clear, as may be seen by comparing Fig. 4 and 6 with each other. The curves have in common only the high peak near their absorption-band, which in the case of the last mentioned salts is situated at about 4950 A.U., in the case of the

newly prepared $\left\{ Co \begin{matrix} (E\ddot{\imath}ne)_2 \\ (l\text{-}Cptdine) \end{matrix} \right\}_D Br_3$, at about 4800 A.U. But the most
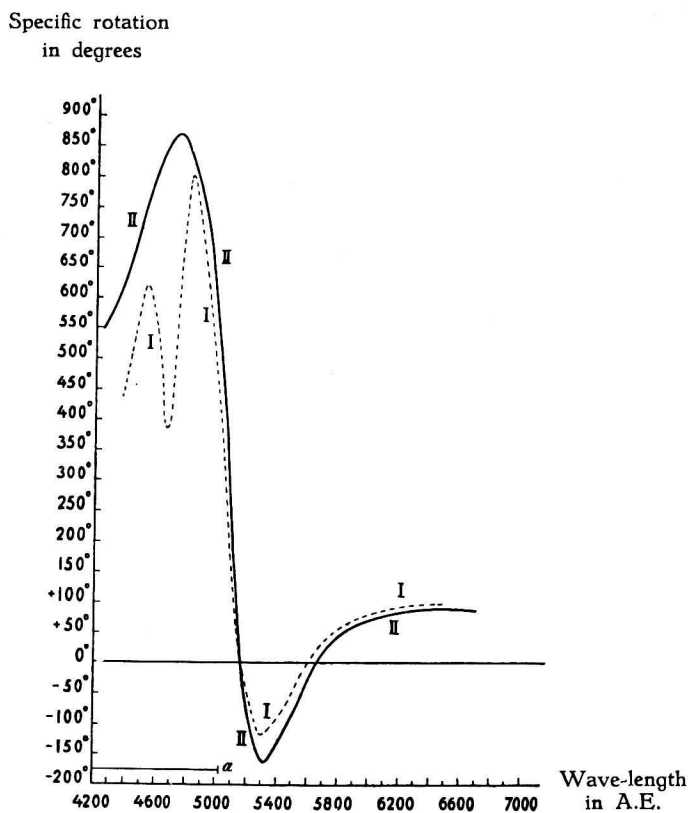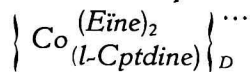
Specific rotation
in degrees

Fig. 6.

Rotatory dispersion (II) of $d\text{-} \left\{ Co \begin{matrix} (E\ddot{\imath}ne)_2 \\ (d\text{-}(Cptdine)) \end{matrix} \right\} Br_3$ and its *Bromo-d-tartr.ite.*

typical difference between the two curves, is the twice passing of the axis of *zero*-rotation in the last case, at about 5200 and 5700 A.U.

§ 7. If now, however, instead of the *racemic* base, the *levo*rotatory component, for instance, be used in the reaction indicated above, then there results an optically-active product, which shows *quite another rotatory dispersion* than that reproduced in Fig. 6. In the first place its specific rotation appears to be much less: the curve in Fig. 7 indicated with *I*, gives the observed values in graphical form. (See Fig. 7). On closer examination it was found, that here there is formed a kind of optically-active *partially racemic* compound, which consists of two optically-active components, which are, however, *no* longer mirror-images of each other. We succeeded in separating from this product, by the aid of *d-tartaric acid*, a *bromo-d-tartrate*, whose rotatory dispersion appeared to be the

same as that of the *bromo-d-tartrate* prepared from the *bromide*, represented in Fig. 6. From this it becomes certain, that one of the components of the partially racemic compound is a salt derived from the ion:

$$\left\vert \; Co \begin{matrix} (E\ddot{\imath}ne)_2 \\ (l\text{-}Cptdine) \end{matrix} \; \right\vert \begin{matrix} \cdots \\ D \end{matrix}$$

Although it appeared impossible, because of the very unfavourable solubility-relations of both components, — even if other substances, as,
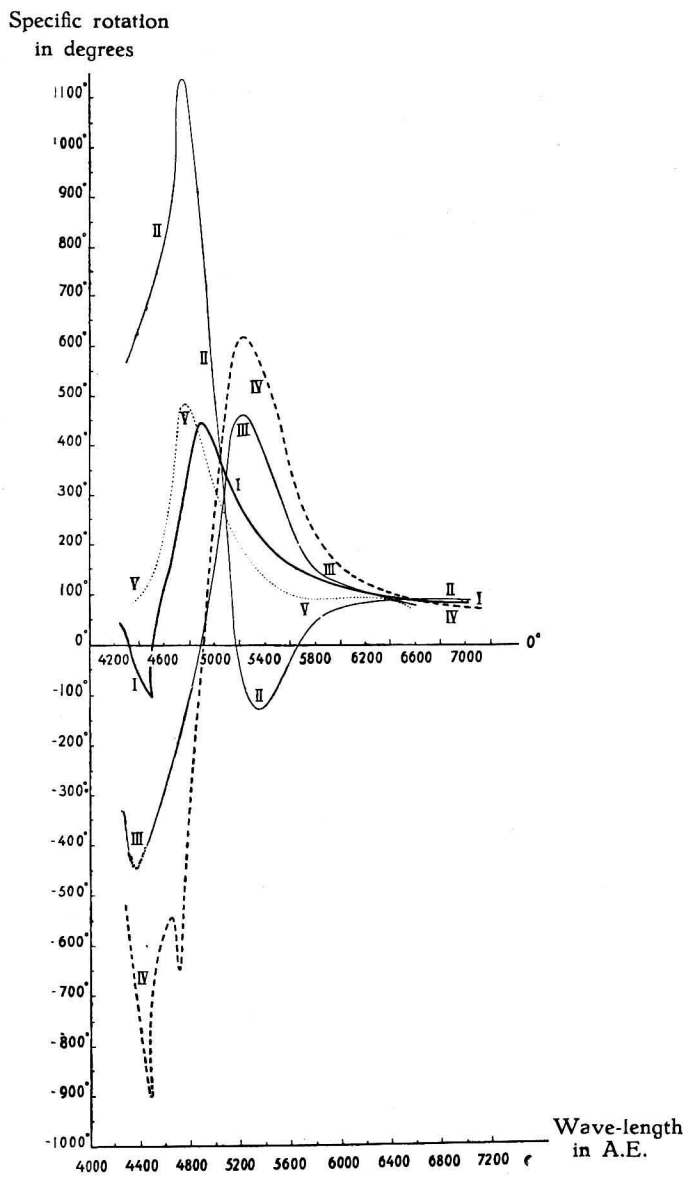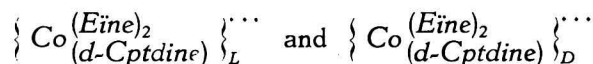
Specific rotation
in degrees

Fig. 7.

Rotatory dispersion of the part. racemic $\left\{ Co \begin{matrix} (E\ddot{\imath}ne)_2 \\ (l\text{-}Cptdine) \end{matrix} \right\} Br_3$ and its components.

for instance, *mandelic acid, malic acid, bromocamphersulfonic acid, α-nitrocamphor*, etc., were used in these experiments, — to obtain the second component in a perfectly pure state, there can be no doubt whatsoever about the fact, that the other component is a derivative of the ion: $\left\{ Co \genfrac{}{}{0pt}{}{(Eïne)_2}{(l\text{-}Cptdine)} \right\}^{\cdots}_{L}$; which, indeed, is *not* the mirror-image of the first.
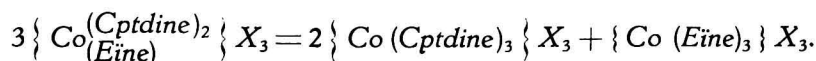
In Fig. 7 we have reproduced sub III the observed curve of rotatory dispersion of this yet impure, second component, while curve IV should represent the theoretically calculated dispersion-curve of this same component in the pure state. This was determined by combination of the curves I and II, of which the last is the true dispersion-curve of the pure first component. Finally the curve V of Fig. 7 represents the curve of rotatory dispersion of the partially racemic compound, as it follows from the combination of the curves II and III: the analogy with curve I is evident, although the inaccuracies in the curve III cause indubitable deviations from the true form of I.

In the same way the reaction between *d-Diaminocyclopentane* and the original *praseo- (violeo-)*-salt, gives a partially-racemic compound, consisting of salts derived from the cations:

$$\left\{ Co \genfrac{}{}{0pt}{}{(Eïne)_2}{(d\text{-}Cptdine)} \right\}^{\cdots}_{L} \quad \text{and} \quad \left\{ Co \genfrac{}{}{0pt}{}{(Eïne)_2}{(d\text{-}Cptdine)} \right\}^{\cdots}_{D}$$

If it would have been possible for us to obtain each of these four components in a perfectly pure condition, we would have been able to obtain, besides four partially racemic compounds also the two optically-*inactive*, true racemic compounds, by combining the antipodes in pairs in aequimolecular quantities, and a racemoid, containing all four components.

§ 8. To prepare the salts of the type: $\left\{ Co \genfrac{}{}{0pt}{}{(Eïne)}{(Cptdine)_2} \right\} Cl_3$ we started from the *praseo- (violeo-)*-salts of the formula: $\left\{ Co \genfrac{}{}{0pt}{}{(Cptdine)_2}{Cl_2} \right\} Cl$, described in the above. With these salts 1 molecule of *ethylenediamine* was made to react under the most varied circumstances of temperature, concentration and in different solvents; but it became soon clear that the salts of the type desired were *not* sufficiently stable to obtain them from solutions, a reaction of the form:

$$3 \left\{ Co \genfrac{}{}{0pt}{}{(Cptdine)_2}{(Eïne)} \right\} X_3 = 2 \left\{ Co \, (Cptdine)_3 \right\} X_3 + \left\{ Co \, (Eïne)_3 \right\} X_3.$$

occurring in each case. In some experiments, — e.g. during our attempts to split the reaction-product into two optically-active components, — we got some indications of the fact, that the salts of the type desired were actually formed as intermediary products; but on recrystallizing the impure mass from solutions, we never obtained other substances than a

mixture of the last mentioned kinds of complex salts. The components were identified in this case by their precipitation as *iodides*, and by accurately studying their crystal-forms.

The manner of transformation in this case, is, once more, perfectly analogous to that formerly observed in the transformation of the *cobalt-salts* of the type cation: $\{Co\,(ddl)\}\cdots$. In both cases it is always the type of ion with a lower degree of symmetry (with one single, polar binary axis), which is replaced by a mixture of two kinds of cations possessing both a much higher symmetry $(D)_3$. One of us[1]) has already drawn attention on a former occasion to the special tendency towards the formation of such complexes of a higher degree of symmetry. The facts stated here give a convincing confirmation of the truth of the views then stated with respect to this matter. It is the significance of the maximum symmetry in questions of the relative stability of such spatial arrangements, that in this case also reduces the number of the theoretically possible isomerides of such complexes to such an extent as was observed here.

§ 9. The experiments with salts of the type: $\left\{Co\,{(Eine)_2 \atop Cl_2}\right\}Cl$, described in this paper, prove, however, clearly that the introduction of a molecule of an optically-active base, e.g. of the *levo*rotatory *Diaminocyclopentane*, can occur as well in a *dextro*-, as in a *levo*rotatory configuration of a cation, in which 2 molecules of *ethylenediamine* are already present. This introduction is, however, impossible, if instead of 2 molecules of *ethylenediamine*, there are originally present, 2 molecules of the optically-active antipode of the substituent. From this it appears once more, that the contrast between a *d-* and *l*-isomeride of the same compound appears to be much more pronounced than that between an optically-active molecule and totally strange substances in those cases, where attempts are made to introduce them all together into the same dissymmetrical spatial configuration. The preliminary presence of such strange molecules, appears to be a much less severe impediment to the entrance of an optically-active substituent, than is produced by the presence of molecules of the same kind, but with enantiomorphic arrangements; — a fact which reminds us altogether of the well-known highly „specific" action of optically-active ferments and enzymes on attackable substrates of enantiomorphous configurations.

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[1]) F. M. JAEGER, Proceed. Kon. Akad. v. Wet. Amsterdam, **29**, (1926), p. 575—579.