

Chemistry. — “On Complex Cobaltic Salts with nine-valent Ions”

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§ 1. If a trivalent pseudo-base B reacts with complex cobaltic salts of the type: $\left\{ \text{Co} \begin{matrix} (\text{Eine})_2 \\ X_2 \end{matrix} \right\} Y$, where X is a negative substituent and Y a monovalent ion, or with those of the type: $\left\{ \text{Co} \begin{matrix} (\text{Eine})_2 \\ X \\ Z \end{matrix} \right\} Y_2$, where Z is an indifferent group ¹⁾, the possibility occurs of getting salts of a new kind of complex ion of the type:



the new complex ion being now nine-valent. It is, of course, necessary in this case, that the pseudo-base B contains three completely equivalent NH_2 -groups; as X_2 or XZ can only be substituted by two groups NH_2 , two molecules of B will then link together three of the original cobaltic complexes. According to some experiments of POPE and MANN ²⁾, *Triaminotriethylamine*: $\text{N}(\text{CH}_2-\text{CH}_2-\text{NH}_2)_3$, although possessing a tertiary N -atom of only feebly basic properties, would occupy *four* coordinative positions in complex salts; a fact, which they proved i.a. by the preparation of some salts of bivalent *nickel* and *platinum* of the type: $\{ \text{Ni}(\text{Triam}) \} (\text{SCN})_2$, and $\{ \text{Pt}(\text{Triam}) \} \text{I}_2$, in which the central metal-atom has the coordination-number *four*. However, in consideration of the fact, that the N -atoms of the three NH_2 -groups of this base exhibit another chemical function than the fourth N -atom, one can foresee the possibility, that the base mentioned might, in the case supposed in the above, eventually react also as a *trivalent* one with respect to its coordinative functions.

It appeared, that *tri-amino-triethylamine* in aqueous solution, reacting with *diethylenediamine-dichloro-cobaltic-chloride* or with *diethylenediamine-chloro-aquo-cobaltic-chloride* or *-sulphate*, gave indeed salts of one of the types mentioned in the above. These compounds are of interest, as well by the very high valency of their complex ions, as by the fact

¹⁾ *Eine* is used in these formulae, as in most cases, as an abbreviation for *ethylenediamine*: $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$; in the same way *Triam* as an abbreviation for *triaminotriethylamine*.

²⁾ F. G. MANN and W. J. POPE, *Chemistry and Industry Review*, **44**, 834, (1925).

that an *uneven* number of the original, — in the case of the *cis*-configurations at least possibly resolvable complex ions, — are linked together. Indeed, salts of the type: $\left\{ \text{Co} \begin{matrix} (\text{Eine})_2 \\ X_2 \end{matrix} \right\} Y$ are, if they have a *cis*-configuration, resolvable into enantiomorphous isomerides, even when both substituents X are identical; the linking together of an *uneven* number of such enantiomorphous complex ions must, therefore, — because they are present in equal numbers in the optically inactive solution, — lead to a number of combinations, which at least will correspond to three different kinds of isomerides. For if the supposition is made that in *triaminotriethylamine* the three radicles: ($-\text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$) and the fourth N -atom are situated in the same plane, and that this situation persists also in the complex ions, then, in the case of the *cis*-configuration, *three* isomerides will be possible (Fig. 1), of which two (1^a and 1^b) possess only a single axis of binary symmetry, while the third (3^a) is completely asymmetrical. As these three isomerides possess merely *axial* symmetry, they must, therefore, be resolvable into enantiomorphous forms, and yield six kinds of optically active molecules.

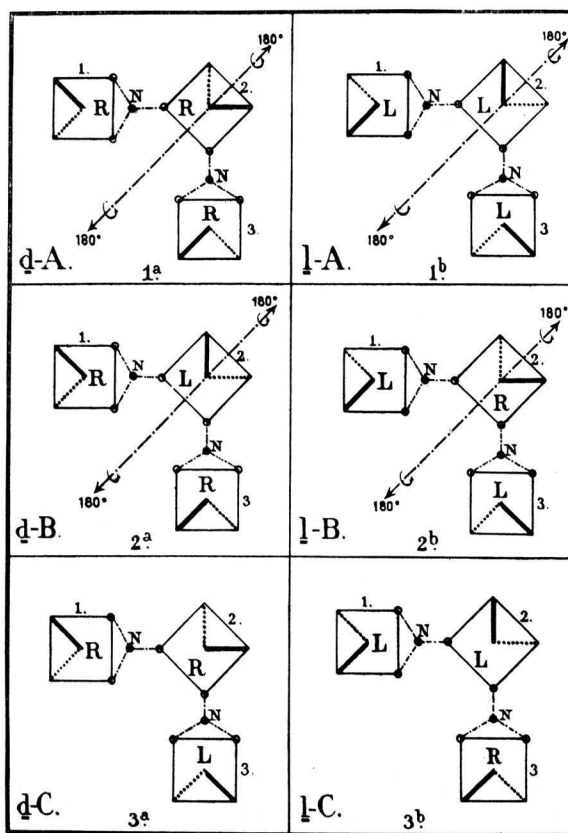


Fig. 1.

If, however, only two of the groups: ($-CH_2 \cdot CH_2 \cdot NH_2$) are situated in the same plane with the fourth N -atom, — the third radicle being situated outside of that plane, — then *six* isomerides (*cis*- and *trans*-forms) are possible (Fig. 2), which all six will be resolvable into optical antipodes.

For in this case each of the thus generated threefold complexes will

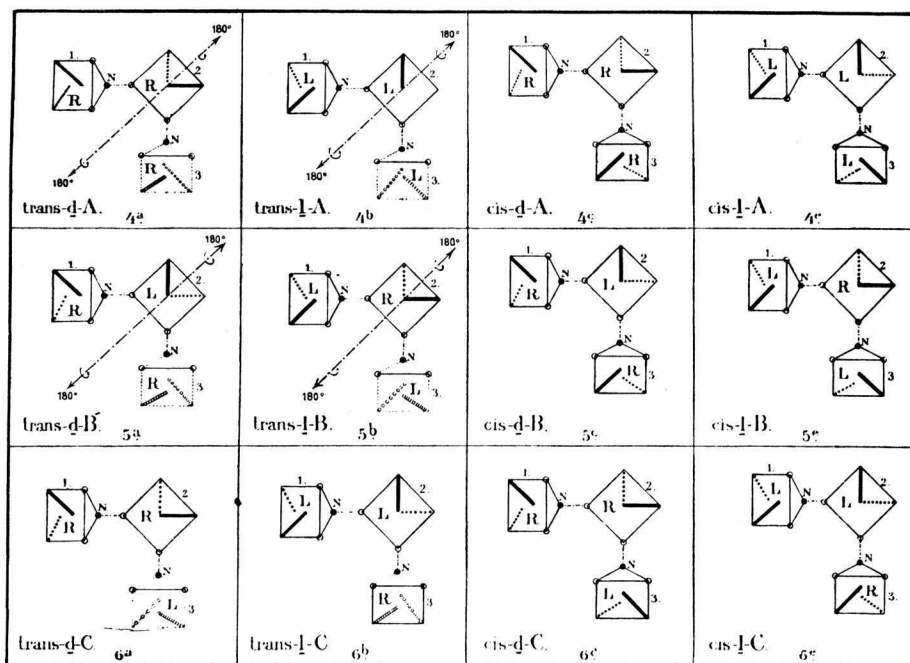


Fig. 2.


possess a spatial configuration differing from its mirror-image; each of these threefold ions, therefore, will represent a racemic compound, which may be resolved into optically active forms. Up till now, however, it was only possible to separate a single homogeneous compound from the reaction-mixture, which opposed to all tentatives of resolving it by means of optically active acids. In this connection it may be remarked, that a threefold complex ion of the second type proposed in the above, can under no circumstances whatsoever be resolved into enantiomorphous forms. In the following also those tentatives will be reviewed, which were made with the purpose of resolving the optically inactive salts obtained.

§ 2. The salts: $\left\{ \text{Co} \begin{matrix} (\text{Eine})_2 \\ \text{Cl}_2 \end{matrix} \right\} \text{Cl}$ (green) and $\left\{ \text{Co} \begin{matrix} (\text{Eine})_2 \\ \text{Cl} \\ \text{H}_2\text{O} \end{matrix} \right\} \text{Cl}_2$ (violet),

from which we started in this investigation, were prepared after the

methods described in literature. The green *praseo*-salt is rapidly changed into the isomeric *cis*-compound when heated in solution; the complex salts of the type here considered, appeared, moreover, to be identical, if prepared by the action of the base either on the green *praseo*- or on the violet *chloro-aquo*-salt. Yet, as we shall see afterwards, the complex salt generated must in reality be a derivative of the isomeric ions in *trans*-configuration.

The *triaminotriethylamine* used in these experiments was prepared after the method published by RISTENPART¹⁾, but varied with respect to its particularities. The original compound used in this synthesis is *β*-*bromo-ethylphtalic-imide*²⁾:

 $\text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Br}$ (Mpt: 82° C.), from

which at a temperature not exceeding 150° C *triphtalyl-triamino-triethyla-*

mine: $\left(\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CO} \\ \text{CO} \end{array} \right\rangle \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \right)_3$ N (Mpt. 187° C.) is prepared by

introducing dry ammonia into the molten mass. This compound is then afterwards split by means of concentrated hydrochloric acid, yielding the desired base in form of its hydrochloride. Now it soon became evident, that the reaction with gaseous ammonia led to the final state only very slowly. We tried, therefore, to get a better yield by prolongation of the time of reaction. The temperature cannot appreciably be elevated, brown decomposition-products being formed as soon as 150° C. is surpassed; these accessory products highly impede the ready crystallisation of the desired compound. It appeared, that after introducing the gaseous NH_3 during 4 hours, a yield of the base of 27 % was obtained; during 8 hours: of 45 %; and during 10 hours: of 65 % of the weight of the *β*-*bromo-ethylphtalic-imide* originally used. A further increase of the time of reaction did not increase the yield of the final product to any appreciable extent. The unchanged *β*-*bromo-ethyl-phtalic-imide* is afterwards separated from the reaction-mass and purified for further use.

In most experiments a slow current of dry NH_3 -gas was during 10 hours introduced into 125 grams of molten *β*-*bromo-ethyl-phtalic-imide*, which was put into a round-bottom vessel, which was heated in a bath of graphite at 140°—150° C. After a short time the content of the vessel becomes viscous, while NH_4Br is separated out, crystallizing partially in the neck of the flask. The reaction being finished, the yet warm product is extracted three times with 80 ccm boiling alcohol of 97 %; the residue is firmly pressed between filter-paper and recrystallised from boiling acetic acid. The recrystallised product melts at 187° C. From the alcoholic

1) E. RISTENPART, Ber. d. d. chem. Ges., 29, 2531, (1896).

2) S. GABRIEL, Ber. d. d. chem. Ges., 21, 566, (1888); 22, 1137, (1889). This compound was prepared by heating 100 grams of the *potassium*-salt of *phtalic-imide* with 399 grams of *ethylene-bromide* during seven hours, and by eliminating the simultaneously formed *ethylene-diphtalic-imide* from the reaction-mixture.

filtrate about 20 grams of β -bromo-ethyl-phthalic-imide, after evaporating to dryness and extracting the solid residu with carbondisulphide, can be separated. The yield of pure triphthalyl-triamino-triethylamine was 75 grams, besides a small amount of its hydrochloride.

The compound thus obtained is inclosed into glass tubes, each containing 25 grams of it and 60 ccm strong hydrochloric acid (sp. gr. : 1,19); the sealed glass-tubes are heated during two hours at 150° C. in a CARIUS-furnace. After cooling, the tubes, on opening, show in most cases only a small over-pressure; their content is diluted with water, the phthalic acid is filtered off, and the filtrate evaporated. The strongly concentrated solution is afterwards mixed with alcohol + ether; the hydrochloride of triaminotriethylamine is in this way soon precipitated in a good crystalline form. The yield of hydrochloride is about 93 % of the calculated quantity.

On slow evaporation of an aqueous solution of the hydrochloride, steep bipyramidal crystals were obtained; analysis gave: 41,73 % Cl and 21,69 % N; calculated for $N(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2)_3, 3\text{HCl}$: 41,59 % Cl and 21,92 % N.

Crystal-form of Triamino-triethylamine-hydrochloride: $N(\text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2 \cdot \text{HCl})_3$.

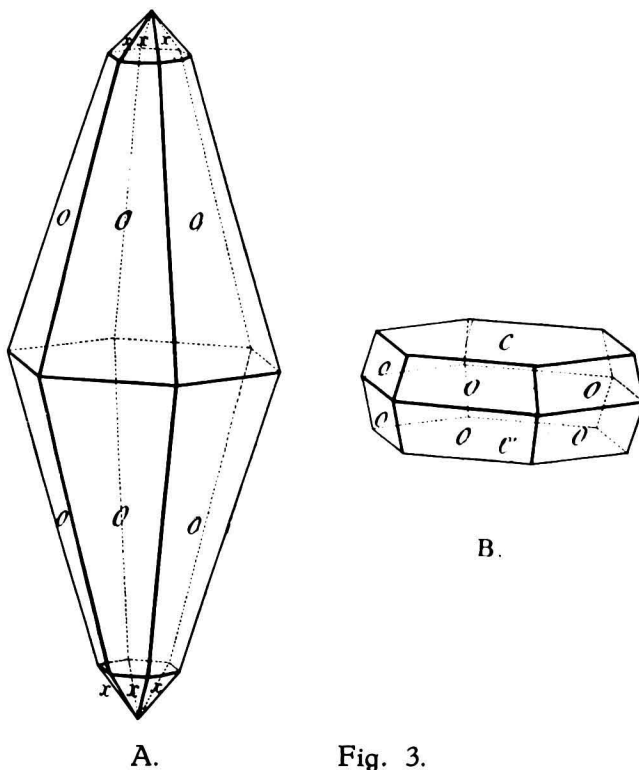


Fig. 3.

From the acid solution in water the compound crystallizes in steep, colourless, often spindle-shaped crystals or hexagonal tables.

Hexagonal-bipyramidal.

$$a : c = 1 : 3,2914.$$

Forms observed: $0 = \{10\bar{1}1\}$, highly lustrous and yielding excellent reflection-images; $x = \{10\bar{1}3\}$, usually absent, always very small and giving dull reflexes. The crystals are well built, but some planes of 0 often show laddershaped projections, as a result of a repeated growth parallel to $\{0001\}$. The angular values in the zone $0 : c$ are, therefore, often inconstant.

<i>Angles:</i>	<i>Observed:</i>	<i>Calculated:</i>
$0 : 0 = (10\bar{1}1) : (01\bar{1}1) = 57^\circ 50'$		—
$0 : 0 = (10\bar{1}1) : (10\bar{1}\bar{1}) = 29^\circ 18' - 29^\circ 50'$		$29^\circ 29'$
$0 : x = (10\bar{1}1) : (10\bar{1}3) = 21^\circ 15'$		$21^\circ 24'$

The optical extinction on 0 is perpendicular and parallel to the edge $0 : c$. Cleavage evidently occurs along $\{0001\}$.

In convergent light the interference-image of an uniaxial crystal is observed, exhibiting no circular polarisation. The double refraction is rather strong and of negative character.

The free base cannot be obtained from the hydrochloride by distilling the solution, after addition of potassiumhydroxide in excess, with steam, the base not being appreciably volatile with water-vapour. The finely powdered salt, mixed with an excess of also finely powdered potassiumhydroxide was, therefore, distilled directly from a silver flask. The pure base boils under ordinary pressure at 265° C.; it is a colourless liquid, which under reduced pressure (15 m.M.) distils at 114° C. From 100 grams of β -bromo-ethyl-phtalic-imide ordinarily about 6 grams of the pure, anhydrous base were obtained. The preparation of the complex salts took place by means of solutions, containing 8—11% of the base.

§ 3. *The preparation of the complex Cobaltic-salts.*

4,8 Grams of $\left\{ \begin{array}{c} \text{Co} \\ \text{Cl} \\ \text{H}_2\text{O} \end{array} \right\} (\text{Eine})_2 \text{Cl}_2$, solved in 50 ccm. water, were during

4 hours heated on the waterbath with 1,53 grams triaminotriethylamine in 8,76% aqueous solution. After evaporating, from the filtered solution finally a chloride was obtained, possessing a slightly more reddish colour than the luteo-salts and having the composition:

$\left\{ \begin{array}{c} \text{Co}_3 \\ (\text{Triam})_2 \end{array} \right\} (\text{Eine})_6 \text{Cl}_9 + 6\text{H}_2\text{O}$, as was proved by analysis.

Analysis: 8,10% H_2O ; 13,75% Co ; 25,61% Cl ; 21,6% N . Calculated for the composition mentioned above: 8,6% H_2O ; 14,01% Co ; 25,34% Cl ; 22,3% N . In the anhydrous salt were found: 14,92% Co ; 27,68% Cl and 24,34% N ; calculated 15,40% Co ; 27,83% Cl and 24,4% N .

If a strong solution of NaI , be added to a concentrated solution of the *chloride*, a pretty orange-coloured *iodide* is precipitated, which after filtering, washing with water, alcohol and ether, appeared to be anhydrous;

it has the composition: $\left\{ Co_3 \begin{matrix} (Eine)_6 \\ (Triam)_2 \end{matrix} \right\} I_9$.

Analysis: 11,26% Co ; 58,03% I ; 14,06% N ; calculated: 11,30% Co ; 57,96% I and 14,21% N .

Besides this compound, also a small quantity of crystals of $\{Co(Eine)_3\} I_3 + 1 H_2O$ was isolated. (See here-after).

Crystal-form of $\left\{ Co_3 \begin{matrix} (Eine)_6 \\ (Triam)_2 \end{matrix} \right\} I_9$.

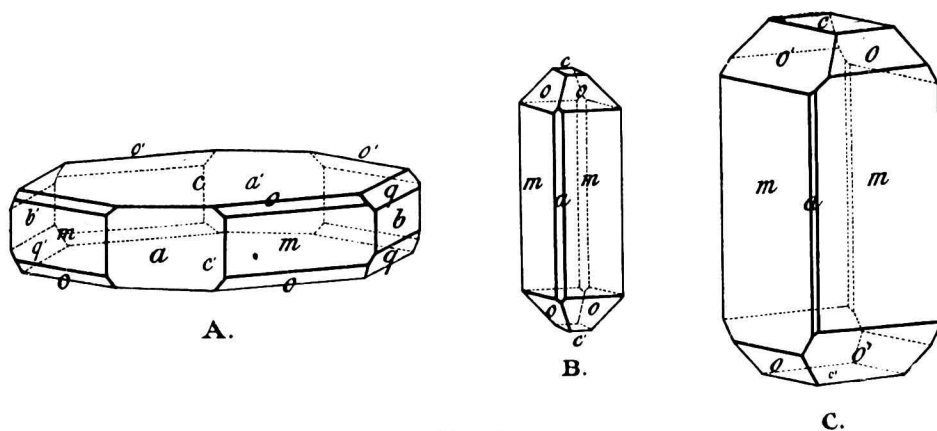


Fig. 4.

On slow evaporation of a solution of the salt in water at room-temperature thick, dark coloured, very lustrous crystals are deposited (Fig. 4^A). From a hot solution, however, on slow cooling long blood-red needles (Fig. 4^B) are obtained.

Rhombic-bisphenoidal.

$$a : b : c = 0,6498 : 1 : 0,9959.$$

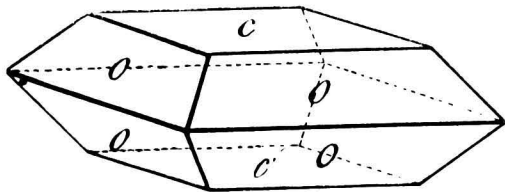
Forms observed: $c = \{001\}$, either predominant or small, as in Fig. 4^B, but always very lustrous. In the larger crystals, the face c appears to be finely striated parallel to $c : b$, giving multiple reflexions. Further: $m = \{110\}$, strongly lustrous; $a = \{100\}$ and $b = \{010\}$, both yielding good images, on b commonly better than on a ; $o = \{111\}$, narrow, always present, giving very sharp reflexions; $o' = \{1\bar{1}1\}$ much broader than o , sometimes equally broad, yielding sharp images; $q = \{021\}$, only present in the larger crystals and then very well reflecting; $\omega = \{1.1.10\}$ and $\omega' = \{1.\bar{1}.10\}$, extremely narrow. The crystals formed at lower temperatures are more tabular parallel to c ; those developed at higher temperatures are more elongated parallel to the c -axis. These

crystals exhibit often, very narrow, $p = \{520\}$ and show a hemihedral habitus. The vertical zône is often badly built; however, in the needle-shaped crystals much better than in those drawn in Fig. 4^A. Rarely very beautifully shaped crystals, as reproduced in Fig. 4^C, were observed. The angular values differ often rather appreciably in different individuals, as this is often observed with mixed crystals.

Angles:	Observed:	Calculated:
$a : m = (100) : (110)$	$=^* 33^\circ 1'$	—
$c : o = (001) : (111)$	$=^* 61 \ 19$	—
$o : m = (111) : (110)$	$= 28 \ 41$	$28^\circ 41'$
$b : m = (010) : (110)$	$= 56 \ 55$	$56 \ 59$
$a : p = (100) : (520)$	$= 14 \ 31$	$14 \ 34$
$c : \omega = (001) : (1.1.10)$	$= 10 \ 24$	$10 \ 21\frac{1}{2}$
$m : p = (110) : (520)$	$= 18 \ 23$	$18 \ 27$
$a : o = (100) : (111)$	$= 42 \ 40$	$42 \ 33\frac{1}{2}$
$c : q = (001) : (021)$	$= 63 \ 21$	$63 \ 20\frac{1}{2}$
$m : q = (110) : (021)$	$= 60 \ 44$	$60 \ 51\frac{1}{2}$
$o : o' = (111) : (\bar{1}\bar{1}1)$	$= 57 \ 15$	$57 \ 6\frac{2}{3}$
$o : o' = (111) : (\bar{1}11)$	$= \text{—}$	$94 \ 43$
$o : \omega = (111) : (1.1.10)$	$= 50 \ 59$	$50 \ 57\frac{1}{2}$

Cleavage parallel to b . On a , m and b everywhere normal extinction: the optical axial plane is $\{001\}$. Strongly dichroitic: on m for vibrations perpendicular to the c -axis blood-red, for those perpendicular to the first: orange-yellow.

From the solution, as already said before, besides this iodide, also small, pyramidal crystals were obtained, which were readily measurable (Fig. 5).



Rhombic-bipyramidal.

$$a : b : c = 0,8538 : 1 : 0,8625.$$

Forms observed: $c = \{001\}$ and $o = \{111\}$, yielding good reflexes; the habitus of the crystals is often apparently hemimorphic.

Fig.5

Angular Values:	Observed:	Calculated:
$c : o = (001) : (111)$	$= 53^\circ 1\frac{1}{2}'$	—
$o : o = (111) : (\bar{1}\bar{1}1)$	$= 62 \ 30$	—
$o : o = (111) : (\bar{1}11)$	$= 74 \ 46$	$74^\circ 50'$

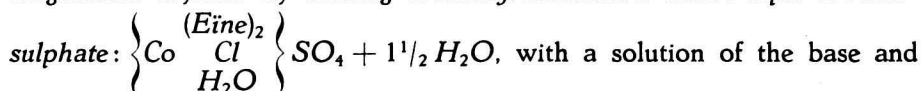
No distinct cleavability was observed.

The axial plane is $\{010\}$, with the c -axis as the first bissectrix. The axial angle is small: no appreciable dichroism.

Evidently these crystals are really identical with those of $\{Co(Eine)_3\}I_3$

+ $1H_2O$. Analysis also showed this to be the case: 59,7 % I; 9,24% Co; and 13,2 % N. This fact proves once more, that, as stated, the complex ion of the *diethylenediamine-chloro-aquo-cobaltic-salts* is partially decomposed, if its solution is boiled with dilute solutions of bases, under formation of the apparently very stable *triethylenediamine-derivatives*.

Also another derivative of the new threefold ion was obtained in magnificent crystals by heating of *diethylenediamine-chloro-aquo-cobaltic-sulphate*:



treating the solution thus prepared with Ag_2SO_4 , for the purpose of eliminating all Cl-ion from the liquid.

If 27,53 grams of the complex sulphate mentioned above be boiled during four hours under reflux with 7,5 grams of the base (in 11 % solution), first a beautifully crystallised salt is deposited, appearing in brown-red octahedral crystals; if the solution after evaporation and after all *chlorosulphates* formed in this reaction are by means of Ag_2SO_4 transformed into *sulphates*, is cooled down to room-temperature, the new salt is readily deposited. Sometimes this salt is also obtained in good quantity, before the solution is treated with Ag_2SO_4 : thus, for instance, in a reaction between 31,7 grams of the *chloro-aquo-sulphate* and 8,64 grams of the base (in 10 % solution), immediately 12 grams of the pure salt were, on cooling, deposited in beautiful, lustrous crystals. It is better, however, to treat the solution first with Ag_2SO_4 so that all Cl-ion is eliminated from the liquid. In that case the new compound is directly obtained in lustrous crystals, besides a mother-liquor B.

The new sulphate was recrystallised several times and then analysed.

Analysis: 5,79% H_2O ; calculated for $\left\{ \text{Co}_3 \begin{array}{c} (\text{Eïne})_6 \\ (\text{Triam})_2 \end{array} \right\}_2 (\text{SO}_4)_9 + 8\text{H}_2\text{O}$: 5,71 % H_2O . In the anhydrous salt was found: 13,71 % Co; 34,28 % (SO_4) ; 22,30 % N; calculated for the anhydrous sulphate: 14,03 % Co; 34,28 % (SO_4) and 22,22 % N.

The cryoscopical determination of the molecular weight gave results, which were in close agreement with the constitution mentioned above. If the sulphate in dilute solution were completely dissociated, each molecule would give 11 ions; therefore, instead of the normal molecular weight: 2666 for the hydrate, or 2522 for the anhydrous salt, — values could be expected to be found in this case, oscillating round 242. Now a solution of 0,4610 grams of the substance in 30,829 grams water, showed a depression of the freezing-point of: $0^\circ,100$ C. The solution contained 1,495 % (or 1,414% of the anhydrous) salt; therefore, the apparent molecular weight is here: 261,6, corresponding to a real molecular weight of 2877. The degree of dissociation α thus would be about 0,85 at this concentration; it seems from conductivity-experiments, that even a lower degree of dissociation is present here.

Some measurements of the electric (molecular) conductivity gave the following results:

Concentration in grams per Liter	Concentration in Mols. per Liter	Dilution in Liters	Specific conductivity ($\times 10^4$)	Mol .con-ductivity ($\times 10^4$)	Degree of dissociation
46.024	0.01879	53.22	22.74	1210	0.43
34.518	0.01295	77.22	18.09	1397	0.50
25.889	0.00971	102.98	14.08	1450	0.52
19.416	0.00728	137.36	11.27	1548	0.55
14.562	0.00546	183.15	8.92	1635	0.59
7.281	0.00273	366.30	4.92	1802	0.65
0.244	0.00009	10989	0.252	2769	1.0

The last mentioned value of the molecular conductivity (2769) may be considered as giving practically the value of the conductivity at an infinite dilution. This number is *extremely high*: for salts with 2 ions, μ_∞ commonly is of the order: 140; for such with 3 ions: 250; for such with 4 ions: 410; for salts with 5 ions: about 560; etc. On extrapolation, — this being, of course, always somewhat hazardous, — for a salt with 6 ions, μ_∞ would be of the order: 750; for those with 8 ions, of the order: 1100; for a salt with 9 ions: about 1400; for such with 10 ions, of the order: 1600; while for salts with 11 ions, the value of μ_∞ would be situated in the neighbourhood of 1800. Uncertain as these data may be, it must be clear in every case, that the number of ions produced here, is abnormally large.

On my demand, professor KRUYT was kind enough to determine the *specific coagulating power* of the complex cation of this new kind of salts, with the purpose to draw nearer conclusions about its valency. The influence of this cation, in the form of its chloride, on a colloidal solution of As_2S_3 , in comparison with that of a *three-* and a *six-*valent cation of analogous constitution, was studied in this respect. It appeared, that while 100 mille-mols of the 6-valent ion were necessary to provoke flocculation, here only 32 mille-mols were sufficient for the same result. From this the conclusion may be drawn, that without any doubt the valency of the new complex ion is in every case *higher than six*. This fact also may serve as an argument to corroborate the conclusion, that the new complex ion is really a *nine-*valent one; moreover, the analysis of the corresponding salts must eliminate all doubt whatever about the correctness of this view.

Crystal-form of Hexa-ethylenediamine-Ditriaminotriethylamine-tricobaltic-sulphate: $\left\{ \text{Co}_3 \begin{matrix} (\text{Eine})_6 \\ (\text{Triam})_2 \end{matrix} \right\} (\text{SO}_4)_9 + 8 \text{H}_2\text{O}$.

This compound crystallizes on slow evaporation from its aqueous solutions

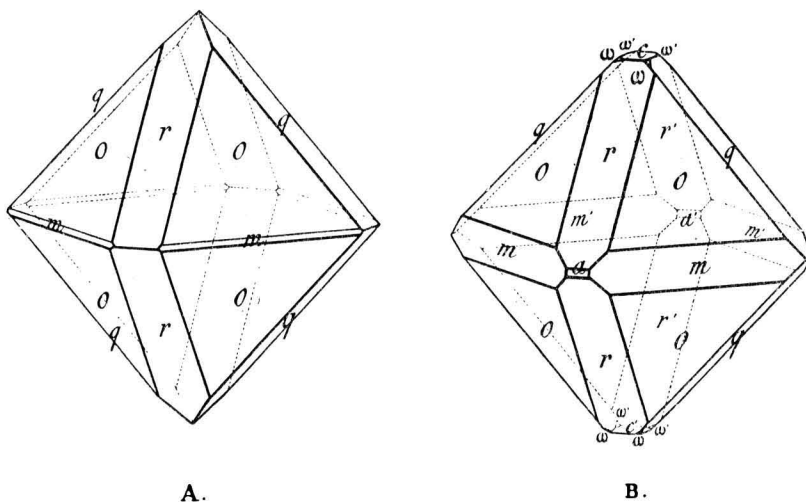


Fig. 6.

in big, brown-red crystals with octahedral habit. They possess very lustrous facets and allow accurate measurements to be made.

Rhombic-bipyramidal; pseudo-tetragonal.

$$a : b : c = 1,0131 : 1 : 1,1277.$$

Forms observed: $o = \{111\}$, large and predominant; $r = \{101\}$ and $q = \{011\}$, broad and lustrous; $m = \{110\}$, narrower but yielding sharp reflexions. Sometimes are found also: $a = \{100\}$, small; $c = \{001\}$, very small; $\omega = \{113\}$, small, but well measurable. The aspect of the crystals is often that of octahedra, combined with a rhombododecahedron; sometimes m is absent, sometimes also a , c and ω are lacking.

Angular Values:	Observed:	Calculated:
$o : q = (111) : (011) =^* 36^\circ 26\frac{1}{4}$		—
$o : m = (111) : (110) =^* 32 15\frac{1}{2}$		—
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) = 73 53\frac{1}{2}$		73' 53'
$o : o = (111) : (\bar{1}\bar{1}1) = 64 32$		64 31
$o : o = (111) : (1\bar{1}\bar{1}) = 72 53$		72 52 $\frac{1}{2}$
$o : r = (111) : (101) = 36 56\frac{1}{2}$		36 56 $\frac{1}{2}$
$r : r = (101) : (10\bar{1}) = 84 4$		83 52
$m : m = (110) : (1\bar{1}0) = 90 46$		90 45
$q : q = (011) : (0\bar{1}1) = 96 45$		96 52
$q : r = (0\bar{1}\bar{1}) : (10\bar{1}) = 63 32$		63 41

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$r : m = (10\bar{1}) : (110) = 58 \quad 28$		58 $29\frac{1}{2}$
$m : q = (110) : (011) = 57 \quad 40$		57 $49\frac{1}{2}$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) = 107 \quad 6\frac{1}{2}$		107 $6\frac{1}{2}$
$c : \omega = (001) : (113) = 27 \quad 48$		27 $50\frac{1}{2}$
$\omega : o = (113) : (111) = 30 \quad 6\frac{1}{2}$		29 54
$a : m = (100) : (110) = 45 \quad 33$		45 $22\frac{1}{2}$
$a : r = (100) : (101) = 42 \quad 2$		41 56
$r : c = (101) : (001) = 48 \quad 8$		48 4

No distinct cleavage was observed.

The crystals are optically biaxial; the axial plane is obviously $\{001\}$, with the b -axis as 1st bissectrix. The double refraction is positive; weak dispersion, with rhombic character and $\rho < v$. The apparent axial angle is rather large. No appreciable dichroism is present.

§ 4. On evaporation at room-temperature the mother-liquor B gave firstly another crop of the crystals described in the above; afterwards it became more and more viscous and gave some fractions consisting of crystals, which on recrystallisation and slow evaporation of their solutions yielded measurable crystals of the form reproduced in Fig. 7.

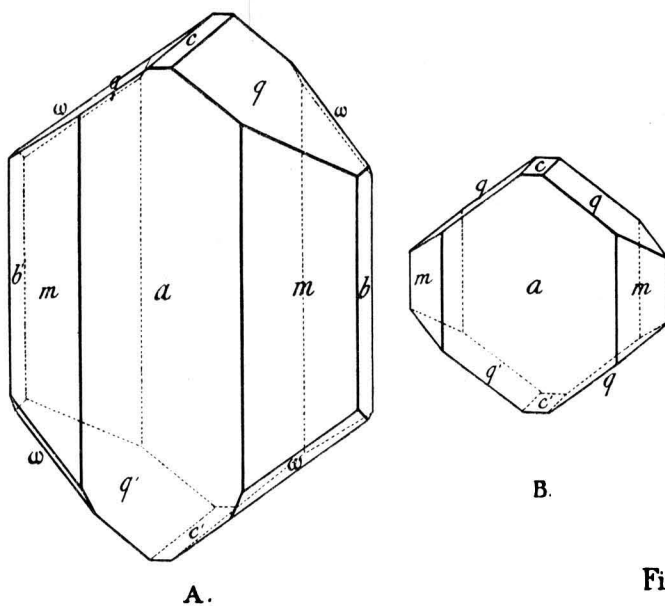


Fig. 7.

Although giving good images, these crystals showed angular values, which were oscillating within rather wide limits:

$$a : c = 83^\circ 18' - 83^\circ 43'.$$

$$a : q = 84^\circ 36' - 84^\circ 58'.$$

$$c : q = 36^\circ 12' - 36^\circ 27',$$

Therefore, the axial ratio of these monoclinic-prismatic crystals varied between:

$$a : b : c = 0,7421 : 1 : 0,7371; \beta = 83^\circ 18'$$

$$\text{and } a : b : c = 0,7415 : 1 : 0,7431; \beta = 83^\circ 43'.$$

They give the impression of being mixed crystals with a varying content of the isomorphous admixtures. Indeed, analysis taught us, that here very probably mixed crystals are present, principally of *triethylene-diamine-cobaltic-sulphate*: $\{\text{Co}(\text{Eine})_3\}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$ with a small quantity of *ditriamino-triethylamine-cobaltic-sulphate*: $\{\text{Co}(\text{Triam})_2\}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$, and probably also of a threefold complex ion with $6\text{H}_2\text{O}$. Analysis gave: 13,2% Co; 35,2% (SO_4) ; 17,0% N in the anhydrous substance, while the hydrate contained: 3,78% H_2O . For the salts already mentioned, the data for the different anhydrous substances are:

$\{\text{Co}(\text{Eine})_3\}_2(\text{SO}_4)_3$:	$\{\text{Co}(\text{Triam})_2\}_2(\text{SO}_4)_3$:	$\{\text{Co}_3(\text{Eine})_6(\text{Triam})_2\}(\text{SO}_4)_9$:
15,40% Co	11,90% Co	14,03% Co
37,60% (SO_4)	29,10% (SO_4)	34,28% (SO_4)
21,90% N	22,70% N	22,22% N
and for $2\text{H}_2\text{O}$: 4,50%	for $2\text{H}_2\text{O}$: 3,50%	for $6\text{H}_2\text{O}$: 4,10%

After fractional crystallisation, renewed determinations gave: 14,6% Co; 36,1% (SO_4) ; 22,0% N; and also: 4,0% H_2O . These data are somewhat closer to the composition of the first mentioned salt than the former. After transformation of the salt into the corresponding *iodide* there, was found in the anhydrous salt: 60,83% I; calculated for $\{\text{Co}(\text{Eine})_3\}_2\text{I}_3$: 61,4% I; the threefold complex salt would have given 58% I, while for $\{\text{Co}(\text{Triam})_2\}_2\text{I}_3$, only: 52% I is calculated.

From the last but one fraction of the mother-liquor also a small amount of a beautifully crystallized *iodide* was deposited, whose analysis gave: 2,89% H_2O , while in the anhydrous substance: 61,81% I was present. Here certainly no other product than $\{\text{Co}(\text{Eine})_3\}_2\text{I}_3 + 1\text{H}_2\text{O}$ has occurred. In a *iodide* from the last mother-liquor, finally, we found: 3,8% H_2O and 56,8% I; so that in this case again undoubtedly a mixture of the last salt with one or more of the other *iodides* must be supposed to have been present.

The measurements of the crystals reproduced in Fig. 7, gave the following results: forms observed: $a = \{100\}$, predominant and highly lustrous; $m = \{110\}$, mostly large and yielding excellent reflexes, but

sometimes smaller; $q = \{011\}$, very lustrous and well developed; $c = \{001\}$, mostly small, but well reflecting; $b = \{010\}$, only narrow; $\omega = \{\bar{1}21\}$, mostly present with only two parallel faces, but yielding excellent images.

Angular Values:	Observed:	Calculated:
$a : c = (100) : (001) = *83^\circ 18' - 83^\circ 43'$		—
$a : m = (100) : (110) = *36 23\frac{1}{2}$		—
$c : q = (001) : (011) = *36 12\frac{1}{2} - 36 27$		—
$q : \omega = (011) : (\bar{1}21) = 36 52$		$36^\circ 51'$
$\omega : m = (\bar{1}21) : (\bar{1}10) = 36 56$		$36 47\frac{1}{2}$
$a : q = (100) : (011) = 84 36 - 84 58$		$84 36 - 84 57$
$m : q = (110) : (011) = 64 45$		$64 57$
$m : q = (\bar{1}10) : (011) = 73 48$		$73 38\frac{1}{2}$
$m : b = (110) : (010) = 53 37\frac{1}{2}$		$53 36\frac{1}{2}$
$b : q = (010) : (011) = 53 33$		$53 33$
$a : \omega = (100) : (\bar{1}21) = 63 22\frac{1}{2}$		$63 25$
$b : \omega = (010) : (\bar{1}21) = 42 7\frac{1}{2}$		$42 4$

No distinct cleavability was stated.

On $\{100\}$ the optical extinction is parallel and perpendicular to $a : m$; the plane of the optical axes is $\{010\}$, while on $\{100\}$ one of the axes emerges at the border of the field of the microscope.

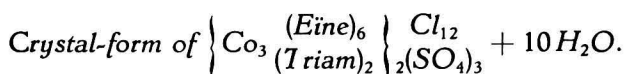
As a control, we prepared some pure *triethylenediamine-cobaltic-sulphate*; however this salt could not be obtained in measurable crystals. As a further argument in favour of the supposition of mixed crystals being produced in this case, also the following data may be taken into account. If a solution of the salt of the threefold complex ion, as it is

obtained in the reaction between *triamino-triethylamine* and $\left\{ \begin{array}{c} (Eine)_2 \\ Co \ Cl \\ H_2O \end{array} \right\} (SO_4)$

$+ 1\frac{1}{2}H_2O$, — is treated with an insufficient¹⁾ quantity of Ag_2SO_4 , then, after crystallisation of the complex sulphate, crystals of a paler coloured compound are deposited from the viscous residual mother-liquor; which crystals, besides (SO_4) , also contain ionogenic chlorine and have according to the analysis, the composition: $\left\{ Co_3 \begin{array}{c} (Eine)_6 \\ (Triam)_2 \end{array} \right\} Cl_{12} + 10 H_2O$.

Analysis: In the anhydrous salt was found: $14,81\%$ Co; $18,1\%$ Cl; $12,5\%$ (SO_4) en $23,92\%$ N; calculated: $14,9\%$ Co; $17,96\%$ Cl; $12,14\%$ (SO_4) ; $23,60\%$ N. In the hydrate itself: $13,77\%$ Co; $16,50\%$ Cl; $11,72\%$ (SO_4) and $6,95\%$ H_2O ; calculated for the above formula: $13,87\%$ Co; $16,68\%$ Cl; $11,30\%$ (SO_4) ; and $7,05\%$ H_2O .

¹⁾ It is very remarkable that these salts manifest such a strong tendency to form *chloro-sulphates*, if circumstances are favourable: in these salts $\frac{2}{3}$ of the ionogenic bonds are substituted by halogen-atoms.



Small, beautifully shaped, very lustrous crystals of a steep rhombohedral habit; they always exhibit the forms R , r and s , and have the paler colour of the *luteo*-salts. (Fig. 8).

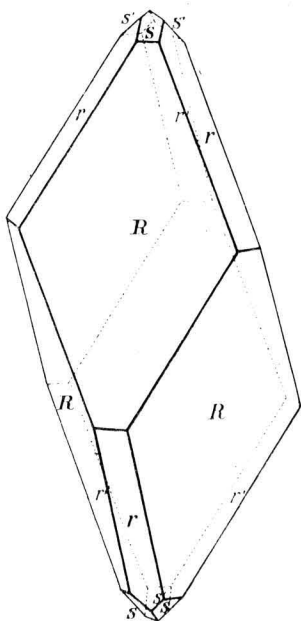


Fig. 8.

Ditrigonal-scalenohedral.

$$\alpha = 51^\circ 10'; a : c = 1 : 3,0114.$$

All three kinds of facets give very sharp reflexes: $R = \{100\} = \{10\bar{1}1\}$, strongly predominant; $r = \{110\} = \{01\bar{1}2\}$, truncating the polar edges of R symmetrically: $s = \{211\} = \{10\bar{1}4\}$, small, but well developed.

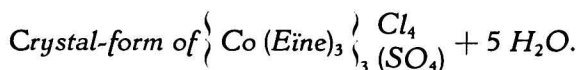
Angular values:	Observed:	Calculated:
$s_1 : s_2 = (211) : (121) = {}^* 69^\circ 21'$		—
$s_1 : r_3 = (211) : (011) = 101 \ 14$		$101^\circ \ 92\frac{2}{3}'$
$R_1 : r_1 = (100) : (110) = 56 \ 15$		$56 \ 20$
$R_1 : R'_2 = (100) : (0\bar{1}0) = 67 \ 30$		$67 \ 20$
$R_1 : s_1 = (100) : (211) = 32 \ 56$		$32 \ 53\frac{1}{3}'$
$R_1 : r'_3 = (100) : (0\bar{1}\bar{1}) = 45 \ 49$		$45 \ 57$
$r_1 : r_2 = (110) : (101) = 51 \ 30$		$51 \ 22$
$r_1 : s_1 = (110) : (211) = 48 \ 42$		$48 \ 39$
$r_1 : r'_2 = (110) : (\bar{1}0\bar{1}) = 82 \ 36$		$82 \ 42$

No distinct cleavability could be found.

A section perpendicular to the optical axis in convergent polarized light exhibits the normal axial image of an uniaxial crystal without circular polarisation. The optical character is negative.

In preparing the *triethylenediamine-cobaltic-sulphate* from the corresponding chloride by means of Ag_2SO_4 , the tendency to form such a *chlorosulphate* of the composition: $\left\{ \text{Co} (\text{Eine})_3 \right\} \left\{ \begin{array}{l} \text{Cl}_4 \\ 2 (\text{SO}_4) \end{array} \right\} + 5 \text{H}_2\text{O}$ manifested itself again very clearly.

Analysis: The hydrate contained: $11,48\% \text{H}_2\text{O}$; calculated for $5\text{H}_2\text{O}$: $11,16\% \text{H}_2\text{O}$. In the anhydrous salt we found: $16,72\% \text{Co}$ and $19,40\% \text{Cl}$; calculated: $16,48\% \text{Co}$ and $19,84\% \text{Cl}$. Also this *chlorosulphate* crystallized exceedingly well (Fig. 9).



The substance appears in beautiful, light-brown, rhombohedral crystals.

Ditrigonal-scalenohedral.

$$\alpha = 51^\circ 0'; a : c = 1 : 3,0285.$$

Forms observed: $R = \{100\} = \{10\bar{1}1\}$, predominant; $r = \{110\} = \{01\bar{1}2\}$, narrow, but sharply reflecting; $s = \{211\} = \{10\bar{1}4\}$, well developed and yielding good reflections.

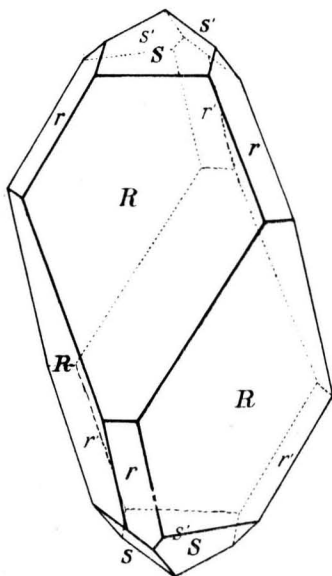


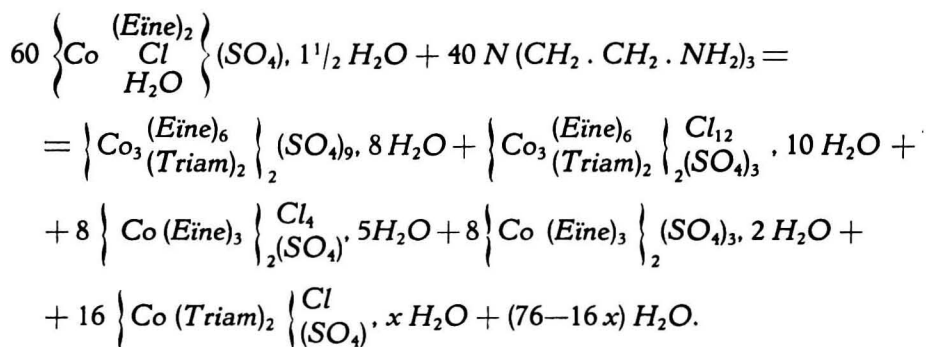
Fig. 9

Angular values:	Observed:	Calculated:
$R : R = (100) : (0\bar{1}0) = * 67^\circ 15\frac{1}{2}'$	—	—
$R : r = (100) : (110) = 56 \quad 22$	$56^\circ 22\frac{1}{4}'$	
$R : s = (100) : (211) = 32 \quad 50$	$32 \quad 53$	
$s : s = (211) : (121) = 69 \quad 36$	$69 \quad 22$	

No distinct cleavability could be stated.

The crystals are uniaxial, negative, without circular polarisation; they are evidently completely isomorphous with the *chlorosulphate* of the threefold complex ion, crystallizing with $10 H_2O$, although the different composition is clear enough by the data of the analysis in both cases. Regarding this isomorphism between both kinds of crystals, it appears highly probable, that also the monoclinic crystals described before, are

really mixed crystals, which for the greater part consist of *triethylenediamine-sulphate*. If, — as from the data of analysis seems highly probable, — in the reaction considered in the above also $\left\{ \text{Co} (\text{Triam})_2 \right\} \left\{ \begin{smallmatrix} \text{Cl} \\ (\text{SO}_4) \end{smallmatrix} \right\}$ is produced, the totality of all reactions might be described by an equation of the form:



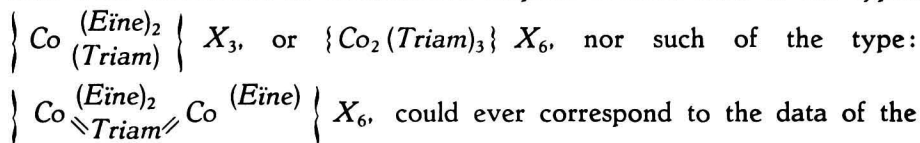
In this equation the fact of the decomposition of the *diethylenediamine-chloro-aquo-cobaltic* ion is simultaneously included. It appears possible to control the exactness of this equation; for if the original solution obtained is treated with Ag_2SO_4 , all compounds present are transformed into the corresponding sulphates. If now all sulphate of the threefold complex ion is allowed to deposit, and then the salts of the

residual mother-liquor is precipitated in the form of *iodides*, the precipitate thus obtained must exclusively consist of $\{Co(Eine)_3\}I_3, 1 H_2O$, because the corresponding salts of the ion: $\{Co(Triam)_2\}^{\dots}$ are so soluble, that they are not precipitated by any reagent, — not even by a solution of *NaI*. According to the equation mentioned above, it should be expected, that the quantity of the salt of the threefold complex ion will be 0,25 of the total weight of the original quantity of the *chloro-aquo*-salt used, while on each gram of the threefold complex salt (as sulphate), 3,83 grams of *triethylene-diamine-cobaltic-jodide* should be generated.

In the experiment itself 6,3 grams *chloro-aquo*-salt were treated in the way described above with 1,73 grams of *triaminotriethylamine* (24 cm³ of a solution) and 50 grams of water, transformed in sulphate by means of Ag_2SO_4 ; then the threefold sulphate was separated from the solution, and the strongly concentrated mother-liquor precipitated with *NaI*.

The recrystallised salts were weighed separately. It was found, that from 6,3 grams of the *chloro-aquo*-salt, 1,65 grams *sulphate* of the threefold complex ion were obtained; and from the mother-liquor 5,90 grams of the *iodide*; calculated: 1,57 grams of the *sulphate* and 6,03 grams of the *iodide*. Considering the inevitable experimental inaccuracies of the method, the given equation represents, therefore, indeed a fairly good scheme of the reaction taking place here.

From the analytical data given in the above, it must be clear, that here no compounds are present of a type to be expected, if the base used were *tetravalent* in coordinative respect. Neither salts of the type:



numerous analyses mentioned above. The nitrogen-determinations are, in first instance, of interest in this respect. Therefore, we think it to be beyond any doubt, that in the type of salts here produced, *tri amino-triethylamine* exhibits the function of a *trivalent*, not of a *tetravalent* substitute in coordinative respect.

§ 5. With the purpose of characterizing somewhat more precisely the derivatives of the new threefold complex ion, we have prepared a series of other salts, e.g.: the corresponding *nitrate*, *chlorate*, *perchlorate*, *iodate*, *rhodanide* and *dithionate*. By double decomposition of the sulphate by means of the *barium*-salts of the corresponding acids, most of these salts may be readily obtained. The *rhodanide* appeared too little soluble, as to obtain other crystals than only microscopically small, brown-red tables; the *iodate*, on the contrary, is much too soluble and its solutions on slow evaporation were always transformed into a brown-red resinous mass, which showed no tendency at all to crystallize. The *chlorate* is also very soluble and crystallizes in thin, scarcely measurable needles.

The rather well soluble *nitrate*, and also the *perchlorate* could, however, be obtained in big, beautiful crystals; the *dithionate*, which is far more soluble in hot water than in cold, was by slow evaporation of its solution finally obtained in well measurable crystals.

All salts were analysed: the *nitrate* appears to contain $4H_2O$, the *perchlorate*: $6H_2O$, and the *dithionate*, notwithstanding its spare solubility in cold water, $18H_2O$. The crystal-forms of these compounds are in the following described in all necessary details.

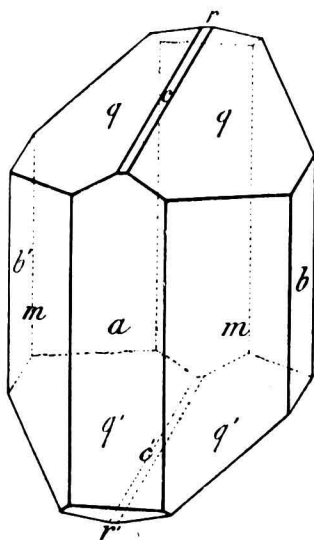
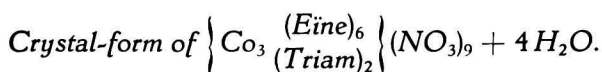


Fig. 10.

From a hot, very concentrated solution of the salt great brown-red crystals are obtained, which have the shape of Fig. 10.

Monoclinic-prismatic.

$$a : b : c = 1,2327 : 1 : 0,5582$$

$$\beta = 64^\circ 34'$$

Forms observed: $a = \{100\}$, $b = \{010\}$, $m = \{110\}$ and $q = \{011\}$, all about equally well developed and yielding good reflections; $r = \{201\}$, smaller than q , but highly lustrous; $c = \{001\}$, extremely narrow, gives feeble images and is often totally absent. The habit is short-prismatic parallel to the c -axis, or somewhat elongated in the direction of the a -axis.

Angular values:	Observed:	Calculated:
$a : m = (100) (110)$	$= *48^\circ 4'$	—
$b : q = (010) (011)$	$= *63 15$	—
$m : q = (110) (010)$	$= *53 46$	—
$q : r = (011) (201)$	$= 57 38$	$57^\circ 41\frac{1}{2}'$
$a : r = (100) (20\bar{1})$	$= 62 19$	$62 12$
$q : q = (011) (0\bar{1}1)$	$= 53 30$	$53 30$
$c : q = (001) (011)$	$= 26 50$	$26 45$
$b : m = (010) (110)$	$= 41 56$	$41 56$
$a : q = (100) (011)$	$= 67 35$	$67 35$
$a : c = (100) (001)$	$= 64 44$	$64 34$
$c : r = (001) (\bar{2}01)$	$= 53 25$	$53 14$

No distinct cleavage was observed.

Analysis gave: $3,68\%$ H_2O ; calculated: $3,75\%$ H_2O .

Crystal-form of $\left\{ \text{Co}_3 \begin{matrix} (\text{Eine})_6 \\ (\text{Triam})_2 \end{matrix} \right\} (\text{ClO}_4)_9 + 6 \text{H}_2\text{O}$.

From a solution of the *perchlorate* in water big crystals are deposited on slow evaporation at room-temperature, which exhibit a long-prismatic, or rarely a tetrahedral, habit. (Fig. 11).

Rhombic-bipyramidal; in some cases with an apparent bisphenoidal development.

$$a : b : c = 1,1750 : 1 : 0,5619.$$

Forms observed: $m = \{110\}$, $r = \{101\}$ and $q = \{011\}$ yield all very sharp images; $p = \{120\}$, however, is very narrow, but well measurable; $a = \{100\}$ is scarcely visible and gives very feeble reflections.

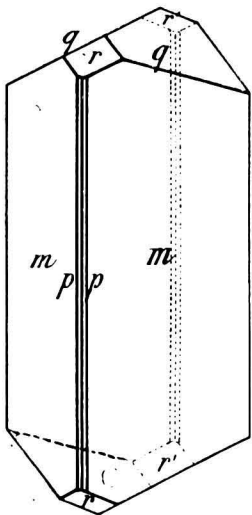


Fig. 11.

Angular Values:	Observed:	Calculated:
$m : r = (110) : (101) = 73^\circ 45\frac{1}{2}'$		—
$m : q = (110) : (011) = 68^\circ 6'$		—
$r : q = (101) : (011) = 38^\circ 8\frac{1}{2}'$		$38^\circ 8\frac{1}{2}'$
$m : m = (110) : (\bar{1}\bar{1}0) = 99^\circ 12'$		$99^\circ 12'$
$q : q = (011) : (0\bar{1}\bar{1}) = 58^\circ 42'$		$58^\circ 40'$
$a : p = (100) : (210) = 30^\circ 43'$		$30^\circ 26'$
$p : m = (210) : (110) = 19^\circ 1'$		$19^\circ 10'$

Sometimes, moreover, a form $\{140\}$, although extremely narrow, was observed. No distinct cleavability could be found.

The optical axial plane is $\{001\}$; on m one of the optical axes is visible. Strongly dichroitic: on m for vibrations parallel to the c -axis yellow, for those perpendicular to it, orange-red.

Analysis gave: 6,00% H_2O ; calculated: 5,91% H_2O .

Crystal-form of $\left\{ \text{Co}_3 \begin{matrix} (\text{Eine})_6 \\ (\text{Triam})_2 \end{matrix} \right\} (\text{S}_2\text{O}_6)_9 + 18 \text{H}_2\text{O}$.

From a cold, saturated solution small, yellow-brown crystals are deposited on slow evaporation, which show lustrous planes. (Fig. 12).

Triclinic-pinacoidal.

$$a : b : c = 1,7232 : 1 : 1,0902.$$

$$\begin{aligned} A &= 108^\circ 16'. & a &= 115^\circ 7\frac{1}{2}'. \\ B &= 117^\circ 53'. & \beta &= 122^\circ 34'. \\ C &= 82^\circ 46'. & \gamma &= 71^\circ 3\frac{1}{3}'. \end{aligned}$$

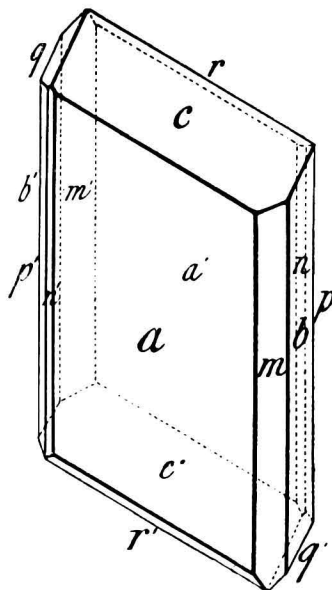


Fig. 12.

Forms observed: $a = \{100\}$, mostly the broadest of all forms and very lustrous; $b = \{010\}$, narrower, but, just as $c = \{001\}$, yielding very sharp reflections; $m = \{110\}$ gives also very good images; $p = \{\bar{1}10\}$ and $n = \{\bar{2}10\}$, extremely narrow and allowing only approximate measurements; $q' = \{0\bar{1}1\}$, narrow, well measurable; $r = \{\bar{1}01\}$ and $s = \{\bar{2}01\}$, extremely narrow, often absent.

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$a : c = (100) : (001) = * 62^\circ 7'$		—
$c : b = (001) : (010) = * 71 44$		—
$a : b = (100) : (010) = * 97 14$		—
$a : m = (100) : (110) = * 63 22$		—
$b : q' = (010) : (0\bar{1}1) = * 55 17$		—
$m : b = (110) : (010) = 33 52$		$33^\circ 52'$
$q' : c' = (0\bar{1}1) : (00\bar{1}) = 52 59$		$52 59$
$b : p = (010) : (\bar{1}10) = 29 30$		$28 13$
$p : n = (\bar{1}10) : (\bar{2}10) = 16 36$		$16 55$
$n : a' = (\bar{2}10) : (\bar{1}00) = 36 40$		$37 38$
$c : r = (001) : (\bar{1}01) = 38 5$		$38 27$
$r : s = (\bar{1}01) : (\bar{2}01) = 31 33$		$31 28$
$s : a = (\bar{2}01) : (\bar{1}00) = 48 15$		$47 58$

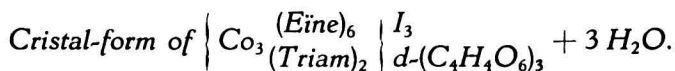
The crystals show no distinct cleavage, but they are very brittle.

Analysis gave: 9,52% H_2O and 11,74% Co ; calculated: 9,47% H_2O and 11,45% Co . In the anhydrous salt was found: 10,58% Co ; calculated: 10,35% Co .

§ 6. In no case any indication of the generation or presence of isomeric salts was ever observed; evidently each product obtained was wholly homogeneous, there being only salts produced of one and the same spatial configuration. However, it was now the question, whether these salts were decomposable into optical antipodes or not; and if so, whether perhaps several racemic salts, — mutually isomorphous in that case, — were giving mixed-crystals of the shapes observed here, or whether these crystals represented really one and the same compound? In the first case, several optically-active compounds would possibly be found as final terms of the fractional crystallisation-experiments; in the latter case, only a single dextrogyratory and a single levogyratory antipode would be met with.

Preliminary experiments first seemed to indicate really the possibility of such a fission by the aid of *d-tartaric acid*; afterwards, however, it could be proved, that this was not the case. For the purpose of executing the fission desired, a quantity of the *sulphate* was first transformed into the *iodide*: $\left\{ \begin{array}{l} Co_3 (Eine)_6 \\ (Triam)_2 \end{array} \right\} I_9$, which was thoroughly purified by repeated crystallisation from hot water.

Totally 28,95 grams of the pure *iodide* were thus obtained and by means of 16 grams pure *silver-d-tartrate* they were transformed into an *iodo-tartrate*, having the composition: $\left\{ \begin{array}{l} \text{Co}_3 (\text{Eïne})_6 \\ (\text{Triam})_2 \end{array} \right\} I_3 (\text{C}_4\text{H}_4\text{O}_6)_3$, because it was shown by preliminary tentatives, that this *iodo-tartrate* amongst all had the greatest power of crystallisation. The solution was concentrated on the water-bath, until it became viscous (about 50 ccm.); after 36 hours, crusts of beautifully lustrous, intergrown, brown-red crystals were deposited, weighing 10,75 grams. Analysis proved them to contain 3 H_2O : 3,23% H_2O ; calculated: 3,19% H_2O . The hydrate contains: 22,6% I ; calculated: 22,3% I . The solution appears to be dextrogyratory.



Beautifully developed, often intergrown and then only occurring in rudimentary individuals, brown-red, very lustrous crystals, showing constant angular values. With some simple magnificent individuals the following measurements were made.

Monoclinic-sphenoidal.

$$a : b : c = 0,7226 : 1 : 0,9192;$$

$$\beta = 56^\circ 35\frac{1}{4}'.$$

Forms observed: $a = \{100\}$, well developed and lustrous; $c = \{001\}$,

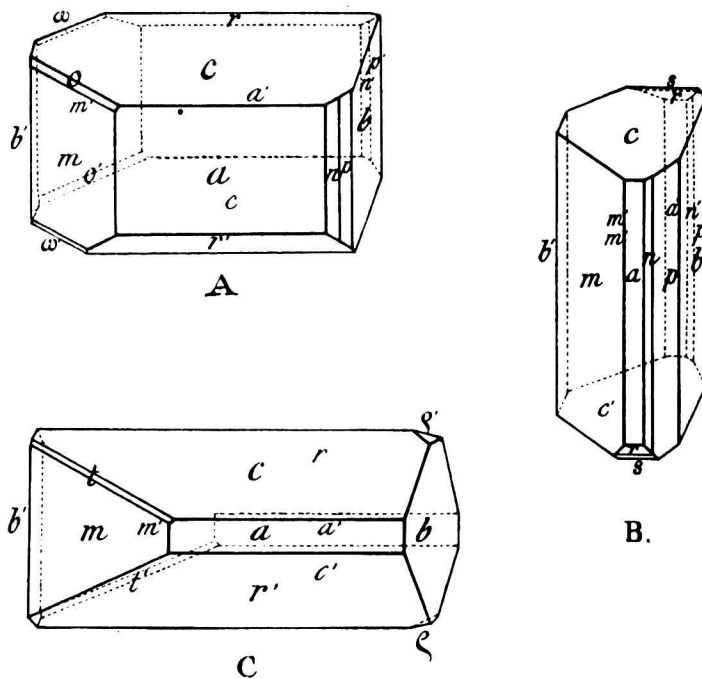


Fig. 13.

large, highly lustrous, yielding ideal images, just as $m = \{\bar{1}10\}$, $b = \{010\}$, broad and very lustrous; $b = \{010\}$, mostly narrow, sometimes broader, but always yielding good reflections; $r = \{\bar{1}01\}$, rather broad and well reflecting; $s = \{\bar{1}02\}$, much narrower than r , often absent, well reflecting; $p = \{120\}$, mostly narrow, sometimes broader, a little dull; $n = \{110\}$, mostly absent, sometimes equally broad as p , yielding sharp reflections, but somewhat duller than m ; $\omega = \{\bar{1}\bar{1}1\}$, often absent, narrow; $o = \{2\bar{2}1\}$, broader than ω , often absent, but yielding good images. The habit of the crystals is rather elongated parallel to the b -axis, or short-prismatic parallel to the c -axis. (Fig. 13).

Angles:	Observed:	Calculated:
$c : m = (001) : (110) =^* 61^\circ 52'$		—
$c : r = (001) : (\bar{1}01) =^* 74 14\frac{3}{4}$		—
$b : m = (0\bar{1}0) : (\bar{1}\bar{1}0) =^* 58 54$		—
$c : a = (001) : (100) = 56 36$		$56^\circ 35\frac{1}{4}'$
$a : r = (\bar{1}00) : (\bar{1}01) = 49 10$		49 10
$a : m = (100) : (\bar{1}10) = 31 13$		31 6
$a : p = (100) : (120) = 50 28$		50 $20\frac{2}{3}$
$b : p = (010) : (120) = 39 44$		39 $39\frac{1}{3}$
$c : s = (001) : (\bar{1}02) = 39 11$		39 $15\frac{1}{4}$
$s : r = (\bar{1}02) : (\bar{1}01) = 35 1$		34 $59\frac{1}{2}$
$m : r = (\bar{1}\bar{1}0) : (\bar{1}01) = 55 56$		55 57
$r : p = (\bar{1}01) : (\bar{1}20) = 65 19$		65 20
$a : n = (100) : (110) = 31 16$		31 6
$n : p = (110) : (120) = 19 12$		19 $14\frac{2}{3}$
$b : o = (0\bar{1}0) : (2\bar{2}1) = 64 19$		64 25
$c : \omega = (001) : (\bar{1}\bar{1}1) = 77 10$		77 $7\frac{1}{4}$
$\omega : m = (\bar{1}\bar{1}1) : (\bar{1}\bar{1}0) = 40 58$		41 $0\frac{3}{4}$
$\rho : b = (11\bar{2}) : (010) = 65 32$		65 26
$\rho : s = (11\bar{2}) : (\bar{1}02) = 24 28$		24 34
$c : t = (001) : (2\bar{2}3) = 29 59$		30 46

Probably cleavable parallel to m .

The salt is appreciably dichroitic: on $\{100\}$ for vibrations parallel to the orthodiagonal, blood-red; for those parallel to the c -axis, orange; on $\{010\}$ for the latter direction of vibration, blood-red; for that perpendicular to it, dark blood-red.

On $\{001\}$ the extinction occurs perpendicularly to the edge: $c : a$; on m oblique to $m : a$, and on $\{010\}$ the angle of extinctions is about 15° with respect to the direction of the c -axis. The optical axial plane is $\{010\}$; inclined dispersion. One axis is visible on $\{100\}$.

In solution this substance exhibits a specific rotation for sodium-light of $+9^\circ,24$; the rotatory dispersion is only small. After crystallisation the compound appeared to be unchanged; first a small quantity of *iodide*

was separated, then again the crystals of Fig. 13. If c and r in these crystals be taken as $\{101\}$ and $\{\bar{1}01\}$, with $a = \{100\}$, $m = \{\bar{1}10\}$, $b = \{0\bar{1}0\}$, etc., then the parameters may be written as:

$$a : b : c = 0,6064 : 1 : 0,4596;$$

$$\beta = 84^\circ 9'.$$

Moreover, the forms: $\rho = \{11\bar{2}\}$ and $t = \{2\bar{2}3\}$ were also found with some of these crystals (old coordinates); they occur only as facets, which are scarcely visible.

The rotation in solution appeared to be the same as before, with only feeble rotatory dispersion, — no fission of the complex ion into antipodes evidently having occurred here. The optical activity of the solution, therefore, results merely from the quantity of *d-tartaric acid*, which is present in the compound in question. Indeed, the *iodide* prepared from this iodotartrate by precipitation by means of *NaI* and recrystallisation, appeared to be optically inactive, — its crystalform being completely identical with that of the *racemic iodide* formerly described. It became evident, that the apparent fission of the complex ion observed in the preliminary experiments needs to be explained wholly by the fission of the admixed *triethylene-diamine-salt* by the *d-tartaric acid*, which salt had been formed in the original reaction. Thus e.g. two slightly levogyrotory fractions were obtained: one of them ($\alpha = -9^\circ, 20'$) was transformed into the corresponding iodide, and from its solution by slow evaporation flat, badly developed crystals were deposited, which appeared to be no other than those of the rhombic *racemic iodide*: $\left\{ \begin{array}{l} \text{C}_{\text{O}_3} (\text{Ei} \text{ne}_6) \\ \text{(Triam}_2) \end{array} \right\} I_9$. Predominant

was $a = \{100\}$; $o = \{111\}$ and $o' = \{\bar{1}\bar{1}\bar{1}\}$ are narrow and about equally developed; further; $m = \{110\}$, also narrow. The crystals were flat and thin, tabular forms parallel to $\{100\}$ and elongated towards the c -axis. Measured angles: $(100) : (111) = 42^\circ 48'$; $(100) : (\bar{1}\bar{1}\bar{1}) = 43^\circ 0'$; $(\bar{1}\bar{1}\bar{1}) : (111) = 94^\circ 23'$; $(100) : (110) = 33^\circ 8'$; etc. The crystals were strongly dichroitic: on $\{100\}$ for vibrations parallel to the c -axis yellow, for those perpendicular to the former, orange. The plane of the optical axes was $\{010\}$, with the a -axis as first bissectrix; the apparent axial angle was only small.

In the same way the so-called *iodo-tartrate* of $\alpha = -2^\circ, 50'$, appeared to be no other than the same rhombic-bisphenoidal *racemic iodide* in an impure state. The crystals manifested the typical hemihedral form, with $o' = \{\bar{1}\bar{1}\bar{1}\}$ much larger than $o = \{111\}$ and with predominant, large faces of $a = \{100\}$, so that they ordinarily appear as oval or lense-shaped individuals, with the forms: $m = \{110\}$ and $c = \{001\}$, very small and $p = \{410\}$, besides those already mentioned. The following angles were measured: $(001) : (111) = (001) : (\bar{1}\bar{1}\bar{1}) = 61^\circ 13'$; $(110) : (111) = (\bar{1}\bar{1}0) : (\bar{1}\bar{1}\bar{1}) = 28^\circ 47'$; $(100) : (111) = 42^\circ 48'$; $(100) :$

: (110) = $33^{\circ} 9'$; (100):(410) = $9^{\circ} 15'$; (111):($\bar{1}\bar{1}\bar{1}$) = $94^{\circ} 24'$. The parameters are, therefore: $a : b : c = 0,6529 : 1 : 0,9957$; the optical properties were the same as already described. In both cases the presence of the also rhombic *triethylenediamine-cobaltic iodide* and of free *d-tartaric acid* could, moreover, be demonstrated. As soon, however, as the *pure* iodotartrate of the threefold complex ion was used in such experiments, no indication of a fission could any more be found.

After all crystals of the salt were deposited and eliminated, the solution of the pure *iodo-tartrate* gave a mother-liquor *B*, which by slow evaporation gradually got more viscous; from it no or only very small crystals were deposited, but finally it was transformed into an almost resinous mass. This product was solved in water and then, by means of *NaI*, transformed into the *iodide*. By fractional crystallisation of the solution some fractions of this iodide were separated and investigated with respect to their crystal-forms, as well as to their optical behaviour. It appeared that the first was identical with that of the racemic iodide; moreover, no appreciable rotation of the solutions could be stated.

Endeavours to split the complex ion by means of *d-bromocamphorsulphonic acid* neither led to any positive result. After the *iodide* was transformed by means of pure *silver-d-bromocamphorsulphonate*, a solution was obtained, which finally yielded a yellow-brownish resinous mass; this could not be obtained in a crystalline form, notwithstanding frequently repeated experiments.

Finally a similar trial was made by means of the *silver-salt* of the optically active *malic acid*. After the *AgI* was removed, the solution on evaporation on the waterbath only gave a homogeneous mass, from which, even after a long time, no crystals were formed.

In no case even the slightest indication could be obtained of a possible inhomogeneity of the salts formed in the original reaction. It is, therefore, highly probable, that no possibility at all of splitting the inactive salt occurs in this case. The only admissible explanation of this behaviour,

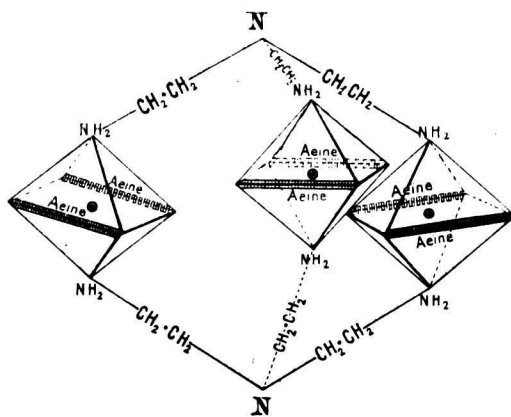


Fig. 14

which can be given, is this, that the complex ion involved has really the configuration: $\left[\begin{array}{c} B \\ \text{Co} \cdots \text{Eine}_2 \\ \ddots \\ B \end{array} \right]_{IX}$ (see fig. 14 p. 82).

In our opinion, it must, therefore, be considered as a derivative of a *trans*-compound of the constitution: $\left\{ \begin{array}{c} (\text{Eine})_2 \\ \text{Co} \quad \text{Cl} \\ \quad \quad \text{H}_2\text{O} \end{array} \right\} X_2$ or $\left\{ \begin{array}{c} (\text{Eine})_2 \\ \text{Co} \quad \text{Cl}_2 \end{array} \right\} X$.

Evidently, there must have occurred a shift of the *ethylenediamine*-molecules into their new positions during the reaction. In connection with this conclusion, it is of interest to remark here, that already in many reactions of this kind, such a shift of the substituents round the central atom of the metal has been observed.¹⁾

For instance: *cis-Diaquo-diethylenediamine-cobaltic-chloride*, on being heated with strong hydrochloric acid, appears to yield *exclusively* the corresponding *trans*-derivative; in the same way, *cis-Rhodanato-diethylenediamine-cobaltic-chloride* gives much more of the *trans*-, than of the expected *cis*-derivative; etc. Also in this case the transition of the one class of compounds into the other need therefore not be considered altogether abnormal.

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¹⁾ A. WERNER, Lieb. Ann. der Chemie, 386, 54, 58, (1912).