

Chemistry. — *On the Relative and Absolute Spatial Configuration of Isomorphous, Optically-active Complex Salts of Trivalent Cobaltum and Rhodium: I. Comparison of the Triethylenediamine- and Tricyclohexanediamine-Salts.* By F. M. JAEGER.

(Communicated at the meeting of December 19, 1936).

§ 1. In recent years the problem concerning the absolute configuration of optically-active ions in complex metallic salts of the *tridiamino-* and *tri-biacido-*type has, from the side of several investigators, met with an increasing interest. The significance of this question is clear, because it is intimately connected with that concerning the role of the central metallic ions, like Cr^{+++} , Co^{+++} , Rh^{+++} , Ir^{+++} , Pt^{++++} , etc. in such compounds and their influence upon the particular manifestation of the often enormous rotatory power, upon the apparently rather capricious phenomena of the rotatory dispersion and the more or less strong circular dichroism exhibited by these remarkable, relatively simply built chemical substances.

WERNER¹⁾, on comparing the properties of the optically-active *triethylenediamine-cobaltic-* and *rhodium-*salts of the type²⁾: $\{Co(Ene)_3\}X_3$ and $\{Rh(Ene)_3\}X_3$, in 1912 drew the conclusion that the replacement of the central *cobaltum-*atom by a *rhodium-*atom and vice-versa in the antipodes having *the same* spatial configuration, evidently was accompanied by a *reversion* of the algebraic sign of the original rotation. As to a general criterium, in how far in such cases one has to deal with ions of really *the same* absolute spatial arrangement, WERNER suggested that *optically-active ions of analogous spatial configurations, if combined with one and the same optically-active substance, always will furnish compounds showing analogous relations of their solubilities.*

Thus, because $\{Co(Ene)_3\}Br_3$, for instance, when being resolved into its antipodes by means of its *bromo-d-tartrates*, yields the *bromo-d-tartrate* of the *dextro*rotatory ion as the *least-soluble* product, whilst $\{Rh(Ene)_3\}Br_3$ under the same circumstances as the *least-soluble bromo-d-tartrate* yields that of the *levogyrotatory* ion, — it follows that the substitution of the *Co-*atom in complex ions of the same spatial architecture by a *Rh-*atom evidently in this special case causes a *reversion* of the direction of the optical rotation. This view can beforehand be considered in so far as rather vague and undefined, as the "rotation" of many of these compounds can as well be positive as negative as a consequence of their special and

¹⁾ A. WERNER, Ber. d. d. chem. Ges., **45**, 1229 (1912).

²⁾ In this paper the diamines introduced into the complex ions are indicated by the abbreviations: (*Ene*) = *ethylenediamine*; (*Cptn*) = *cyclopentanediamine*; (*Chxn*) = *cyclohexanediamine*; etc.

often highly deviating rotatory dispersion for different wave-lengths; whilst it can hardly be stated which special wavelengths are to be considered as really "corresponding" ones for the purpose of comparison of the complex salts of different series. But besides this, also other objections can be advanced against the said conclusion, to which the present author has already drawn attention¹⁾ in 1917. The *general* applicability of WERNER'S solubility-rule as stated above, can also be doubted because of the fact that the "solubility" is a highly complicated property of matter which depends on many other factors, besides spatial configuration. Therefore, the view was suggested that as a final criterium in such questions the crystallographical relations between the compounds compared might more advantageously be used, because the crystalform is a property highly sensitive to any change of spatial configuration and in this connection thus might be considered as a more reliable phenomenon; and this in the present case the more so, as for the Co^{+++} - and Rh^{+++} -compounds considered, the rigorous *isomorphous* replacement of the two metals there-in was previously demonstrated as well in the case of the racemic, as in that of the optically-active salts of the two series. Since that time this view has, on several occasions, been contested by a number of authors on this subject²⁾ and, — at least in the case of the *triethylenediamine*-salts, — evidently with success. But notwithstanding this, the problem yet appears to be not completely settled in all its aspects, as will become clear from the present paper. Now several series of compounds of this kind have been investigated in this laboratory, so that we can now much better survey the complete experimental material. The time, therefore, has come for making a tentative to rightly co-ordinate the different data obtained, in the hope that, by a detailed and systematic discussion of them, a clearer insight into the prevailing relations may be gained.

§ 2. The experiments to be discussed relate to the introduction of the bases: *ethylenediamine*, racemic and *d*- and *l*-*cyclohexanediamine*³⁾ racemic, *d*- and *l*-*cyclopentanediamine*⁴⁾, racemic, *d*- and *l*- β -2-4-*norm. pentane-diamine*⁵⁾ and α -2-4-(*meso*)-*norm. pentanediamine*⁵⁾ into the

¹⁾ F. M. JAEGER, Chem. Weekbl., **14**, 718 (1917); Rec. d. Trav. d. Chim. d. Pays-Bas, **38**, 171 (1919); Rev. génér. des Sciences, **30**, 298 (1919); Confér. dev. la Soc. chim. de France, Bull. d. la Soc. chim. (4), **27**, (1920), 173; *Lectures on the Principle of Symmetry*, 2nd Ed., 251 (1920); *Le Principe de Symétrie*, Paris, 294 (1924); *Spatial Arrangements of Atomic Systems and Optical Activity*, New York, 92 (1930); cf. also: J. MEISENHEIMER, etc., Ann. d. Chem., **449**, 190 (1926).

²⁾ M. DÉLÉPINE, Bull. Soc. chim. de France, (4), **55**, 1256, 1226 (1934); M. DÉLÉPINE and R. CHARONNAT, Bull. Soc. minéral. franç., **53**, 73 (1930); W. KUHN and K. BEIN, Zeits. f. anorg. Chem., **216**, 323, 335, 336 (1934) etc.

³⁾ In a finished but not yet published paper with L. BIJKERK.

⁴⁾ F. M. JAEGER and H. B. BLUMENDAL, Zeits. f. anorg. Chem., **175**, 197, 203, 214, 215, 228 (1928); etc.

⁵⁾ C. J. DIPPEL and F. M. JAEGER, Rec. d. Trav. d. Chim. d. Pays-Bas, **50**, 547 (1931).

complex ions. In this paper, chiefly salts will be compared which are derived from *ethylenediamine* and *cyclohexanediamine* and which in all cases correspond to the *least-soluble chloro-* or *bromo-d-tartrates* used in the fission-experiments, so as to facilitate the general survey of the facts and to prevent confusion. The corresponding *cyclopentanediamine*-salts will be treated in the following paper. The prefixes *d-* and *l-* will be used to denote the *dextro-* and *levogyrotory* antipodes of the optically-active *diamines* used; the prefixes *D-* and *L-* to denote the rotation of the resolved (complex) ions *in the red part* of the visible spectrum, without regarding the occasional change of the sign of the rotation for other wave-lengths.

Then it must be borne in mind that in all cases where three identical molecules of an optically-active *diamine* were introduced into the complex ions, we always stated the fact first observed by SMIRNOFF¹⁾ (with optically-active *α-propylenediamine*), that in these reactions a typical *dissymmetrical* synthesis takes place, so that of all theoretically imaginable isomerides exclusively only *two* are produced: thus, of all isomerides imaginable when *d-* or *l-cyclopentane-* or *cyclohexanediamines* are used, *only* the combinations: $D-\{Co(l-Cptn)_3\}^{***}$, $L-\{Co(d-Cptn)_3\}^{***}$, $D-\{Rh(l-Chxn)_3\}^{**}$, $L-\{Rh(d-Chxn)_3\}^{***}$, etc. prove to be generated in these reactions, with a yield of 100 %, — as well in the *Co-*, as in the *Rh-series*. All other combinations: $D-\{(d_3)\}^{***}$, $L-\{(l_3)\}^{***}$, also: $\{d_2l\}^{***}$ or $\{dl_2\}^{***}$, — be it in *D-* or *L-*ions, — seem to be excluded in this kind of syntheses. In several cases the *instability* of the latter combinations could directly be demonstrated by their subsequent rapid decomposition in solution, for instance, according to the equation: $3\{d_2l\}^{***} \rightarrow [\{d_3\}^{***} + \{l_3\}^{***}] + \{d_3\}^{***}$; etc. Moreover, in all cases it could be proved by means of crystallographical evidence, that the *racemic* compounds of the series investigated *exclusively* exist of combinations of equal numbers of molecules of the types: $D-\{(l_3)\}^{***}$ and $L-\{(d_3)\}^{***}$; this demonstration could be made, because the crystallographical character of all the racemates here investigated is *quite different* from that of the composing optically-active compounds and their formation thus could rigorously be verified in all prevailing cases. When desired, these facts were still controlled afterwards by means of *X-ray powder-spectrograms*.

§ 3. A second fact which must be kept in mind is that, which was first emphasized by TSCHUGAEFF and SOKOLOW²⁾ in the case of *α-propylenediamine-derivatives*; namely, that the contribution of the optically-active *diamines* to the rotation of the complex salts into which they are introduced, appears not only *much greater* than that of the free bases, but always *to have the opposite algebraic sign*. Thus, for instance,

¹⁾ A. P. SMIRNOFF, *Helv. Acta Chim.*, **3**, 178 (1920).

²⁾ L. TSCHUGAEFF and W. SOKOLOW, *Ber. d. d. chem. Ges.*, **40**, 3464 (1907); **42**, 57 (1909).

$\{Rh(d-Base)_3\}X_3$ is strongly *levogyrotory*, $\{Rh(l-Base)_3\}X_3$ is *dextrogyrotory*, etc.

On the other hand, the relatively high situation of the curve IV in Fig. 4 with respect to the curve I for *L-triethylenediamine-rhodium-chloride*, makes it highly probable that also in the *levogyrotory tri-β-2-4-norm. pentanediamine-rhodium-salt*, — which has the constitution: $L-\{Rh(l-Base)_3\}Cl_3$, — the contribution to the rotation of the complex salt is in reality *positive*, i.e. also *opposite* to that of the free base involved.

§ 4. As to the *least-soluble chloro- or bromo-d-tartrates* used in the fission of the racemic compounds here considered and to the *chlorides or bromides* isolated from them, the following experiences were gathered.

1. In the case of the *triethylenediamine*-compounds of Co and Rh the *least-soluble chloro- and bromo-d-tartrates* correspond to $D-\{Co(En)_3\}X_3$ and to $L-\{Rh(En)_3\}X_3$.

2. In the case of the *tricyclohexanediamine*-compounds of the two series the *least-soluble chloro- and bromo-d-tartrates* proved to correspond to $L-\{Co(d-Chxn)_3\}X_3$ and to $L-\{Rh(d-Chxn)_3\}X_3$. In this case their constitution was rigorously proved by their direct synthesis from the optically-active diamines and their subsequent destruction, — after which the rotation of the isolated base was determined.

§ 5. By means of DÉLÉPINE's elegant method of "optically-active racemates" it was stated:

1A. From a mixed solution of an equal number of molecules of $L-\{Co(En)_3\}Br_3$ and $L-\{Rh(En)_3\}Br_3$ crystal aggregates were obtained consisting of very small, rhombohedral crystals which, on X-ray-examination, yielded spectrograms which were identical with those of the *ditrigonal racemic* compounds. Later-on, some single crystals were deposited from the mother-liquor, which showed the form of the racemic compound: $c = \{0001\}$; $m = \{10\bar{1}0\}$ and $r = \{10\bar{1}1\}$, with $c : r = 37^\circ 52'$ and $a : c = 1 : 0,673$. From an analogous mixture of $D-\{Co(En)_3\}Br_3$ and $L-\{Rh(En)_3\}Br_3$ also multiple aggregations, but this time consisting of *mixed crystals*, were obtained which, on X-ray-examination, yielded the spectrograms of the *tetragonal antipodes*¹⁾. From this the conclusion must be drawn that the L-salts of Co and Rh in this case have *enantiomorphous*, the L- and D-salts of both series, however, *the same* spatial configurations. These results thus completely confirm those of DÉLÉPINE.

2A. From a mixed solution of equimolar quantities of $L-\{Co(d-Chxn)_3\}Br_3$ and of $L-\{Rh(d-Chxn)_3\}Br_3$ very beautiful, transparent, orange-coloured *mixed crystals* were deposited of *hexagonal-pyramidal*

¹⁾ At this moment Mr. J. TER BERG is occupied in this laboratory with an X-ray-examination of a number of racemic and optically-active *triethylenediamine-cobaltic- and rhodium-salts*; so that now we have already a series of X-ray-spectrograms at our disposal which enable us rapidly to compare such salts in cases like this.

symmetry (Fig. 1A); on the contrary, from a mixed solution of D - $\{Co(l-Chxn)_3\}Br_3$ and L - $\{Rh(d-Chxn)_3\}Br_3$ pale yellow needles with the typical ditetragonal-bipyramidal symmetry of the racemic compound (Fig. 1B)

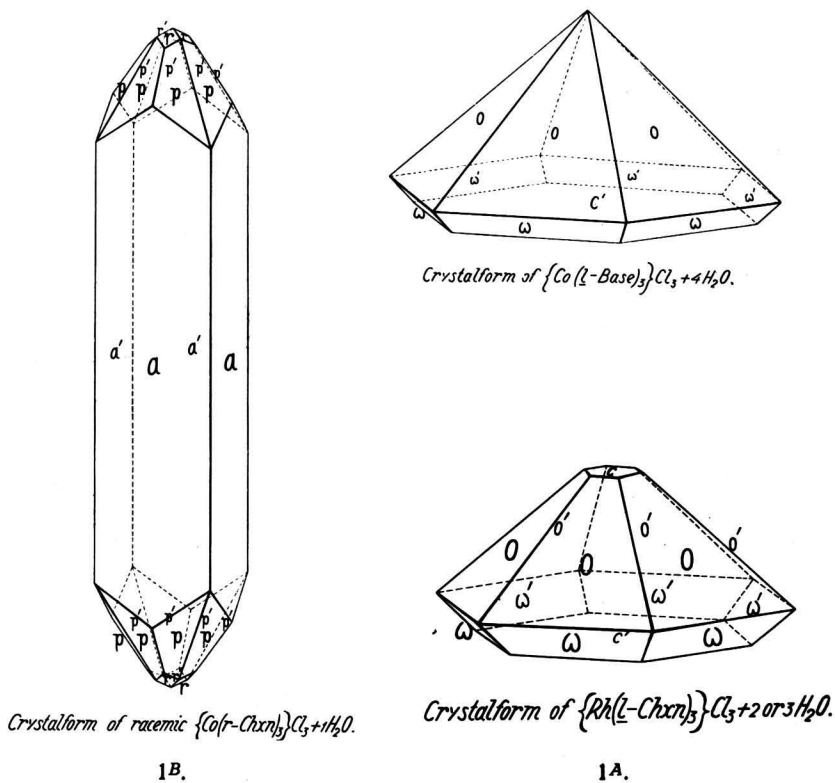


Fig. 1. Crystal forms of the optically-active and of the racemic Tricyclohexanediamine-salts of Cobaltum and Rhodium.

were obtained. These facts prove beyond any doubt, that the L -salts of the two series have the same, the D - and L -salts, however, enantiomorphous spatial configurations.

Whilst, therefore, in the case 1) of the triethylenediamine-salts the compounds of Co and of Rh with the same spatial arrangements exhibit opposite optical rotations, in the case 2) they apparently have rotations of the same algebraic sign in the red part of the spectrum. If, therefore, WERNER'S solubility-rule holds, even then the rotations observed apparently are in the two cases not in agreement with each other.

§ 6. For the purpose of a comparison of the rotatory dispersions of these salts and especially for that of the different dispersion-curves obtained with those of the D - and L -triethylenediamine-salts of cobaltum and rhodium, — which, as relating to an optically-inactive base, will be used as standards of reference, — the data for the rotatory dispersion of these salts were once more exactly determined by new measurements and are graphically represented in Fig. 2 and in Fig. 4 respectively.

Moreover, the corresponding data relating to the salts: *monoethyl-enediamine-d-d-cyclohexanediamine-cobaltic-chloride*; to *diethylene-*

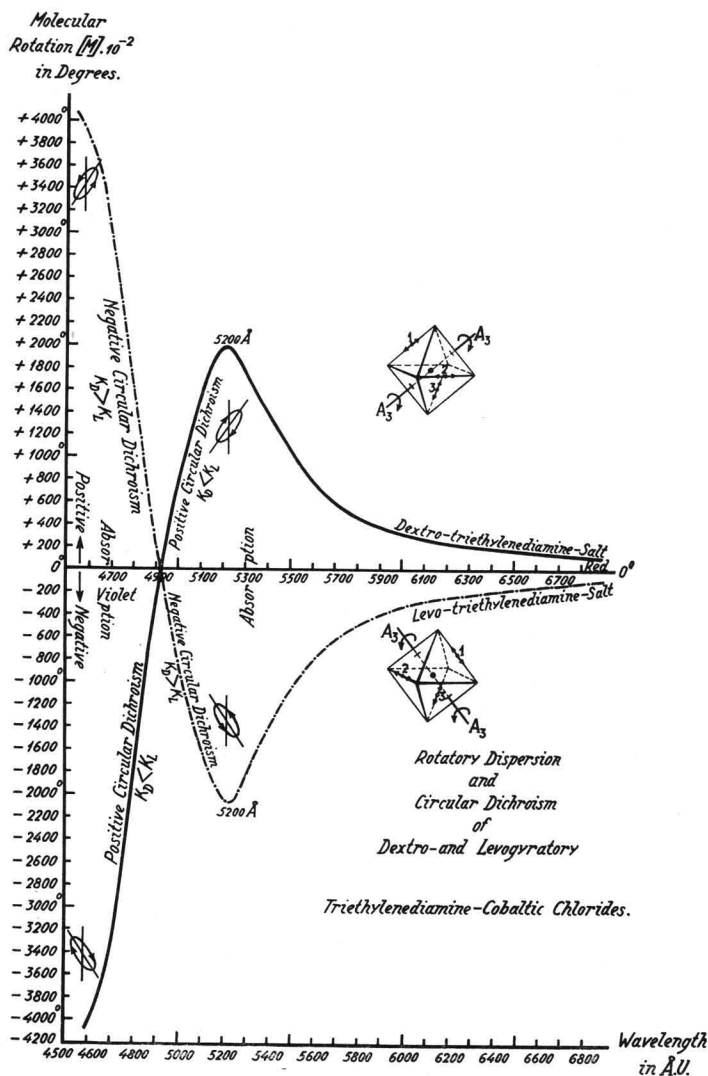


Fig. 2. Rotatory Dispersion of D- and L-Triethylenediamine-Cobaltic-Chloride.

diamine-mono-d-cyclohexanediamine-cobaltic-chloride and to *tri-d-cyclohexanediamine-cobaltic-chloride*, are represented in the graph of Fig. 3.

All these salts correspond to the *least soluble chloro- or bromo-tartrates* and their special constitution was proved by direct, dissymmetrical synthesis, starting from the optically-active bases. They represent *triethylenediamine-salts* in which *one, two and all three* molecules of the base are consecutively substituted by 1, 2 or 3 molecules of the *dextrogyatory cyclohexanediamine*.

Their dispersion-curves I—III represented in the corresponding graph of Fig. 3, in which simultaneously the dispersion-curve of *dextrogyatory*

$\{\text{Co}(\text{Ene})_3\}\text{Cl}_3$ is inserted, will be discussed in detail in connection with the different dispersion of the *rhodium*-salts to be found in Fig. 4. All the numerical data required for the construction of these graphs will later-on be published elsewhere.

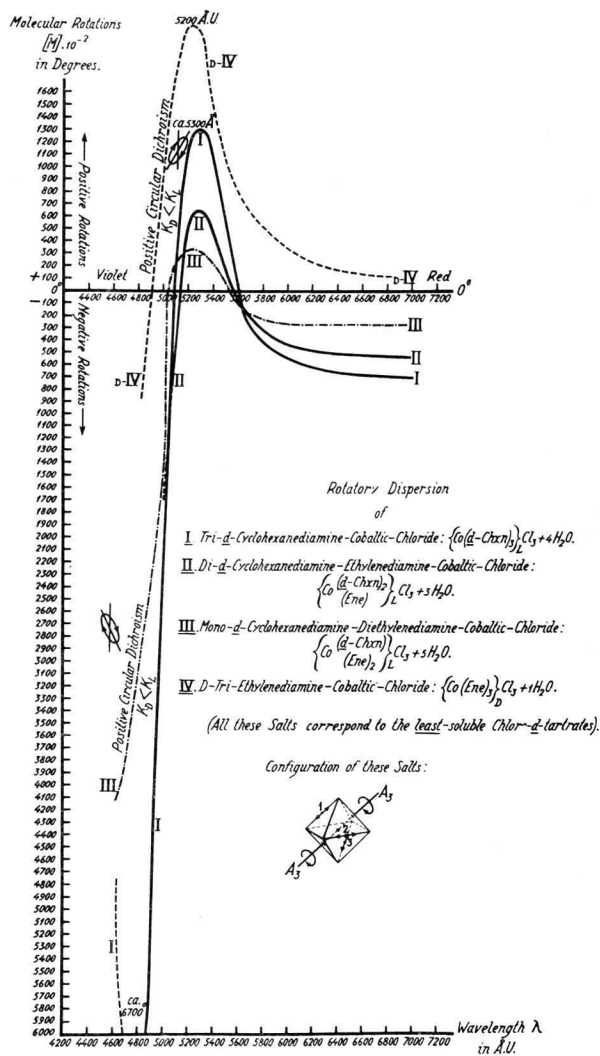


Fig. 3. Rotatory Dispersion of Cyclohexanediamine- and Ethylenediamine-Cobaltic-Salts¹⁾.

§ 7. For the right comparison of these curves, we will start with those represented in Fig. 3.

Evidently the curves I, II, and III prove, that the 1, 2, or 3 molecules of the *dextrogyratory* base present in these complexes, influence their optical rotation in a way which is almost identical with a simple *optical*

¹⁾ See about the notation *L*- in this figure, the Note ¹⁾ at the bottom of the next page.

superposition of their action. If, now, it be kept in mind that this action is *levogyrotory*, — it immediately becomes clear that the rotation due to the complex ion itself may approximately be estimated by a proportional shift upwards of these dispersion-curves. Then, however, there can be no doubt any longer *that all these curves are closely related to that of the dextrogyrotory triethylenediamine-cobaltic-chloride* with its *positive* circular dichroism. Because of the *levogyrotory* influence of the molecules of the *d*-base introduced, the first maximum (at about 5300 A.U.) in the curves I, II, and III has apparently become *lower*, whilst for the same reason the minimum (between 4600 and 4700 A.U.) has got *deeper*: this partially is the cause of the strong *asymmetry* of the three curves with respect to the line of zero-rotation. Exactly as in the case of the *triethylenediamine-salt*, — all the other ones have, — notwithstanding this asymmetry, — yet preserved the *positive* character of their COTTON-effect.

Now KUHN and BEIN¹⁾ some years ago first drew attention to the possible significance of the algebraic sign of the circular dichroism in the absorption-band nearest to the red end of the spectrum for answering the question about the *absolute* spatial configuration of such optically-active compounds. By means of a simplified model in which peripheral oscillations *coupled* with those at the central atom, are taking place in three planes perpendicular to each other, they thought to be able to make it probable, that such complex ions like that of *dextrogyrotory triethylenediamine-cobaltic-chloride* would have the spatial arrangement indicated by the octahedron-scheme in Fig. 2, if certain suppositions be made about the polarisation of the vibrating, electrically charged parts of the ion and the possibility of at least establishing the algebraic sign of the electrical momenta occurring in the adjacent parts of the molecule. *The same* configuration then must, of course, be attributed to the three other salts here studied, as they evidently all are derived from the *dextrogyrotory triethylenediamine-ion* and they all have a circular dichroism of the same positive character²⁾.

But previously (§ 4; sub 2) and 2A) we have demonstrated that these salts (*L-cobaltum-*) have *the same* configurations as the *L-rhodium-salts* of the series; therefore, the *levogyrotory* $\{Rh(d-Chxn)_3\}Cl_3$ necessarily must have *the same* absolute configuration of its constituents as the salt: *L*- $\{Co(d-Chxn)_3\}Cl_3$ just mentioned. The *Rh-salt* is strongly *levogyrotory* and evidently, even after a suitable shift upwards, its dispersion-curve in the

1) W. KUHN and K. BEIN, Zeits. f. anorg. Chem., 216, 323, 335 (1934); Zeits. f. phys. Chem., B. 24, 335 (1934).

2) These salts, although accidentally *levogyrotory* in the red part of the spectrum and even in the greater part of the visible spectrum, must, therefore, more properly be designed as *D-salts* instead of *L-salts*. As we have, however, in our previous papers always denoted the *D-* or *L-*character with respect to the direction of the rotation of the complex in the *red* part of the spectrum, we here have preserved the old notation in order to prevent confusion.

whole visible part of the spectrum certainly still will remain below the zero-line, — just as in the case of the *levogyrotory triethylenediamine-rhodium-chloride* ¹⁾, which as we formerly have stated, also has the same spatial

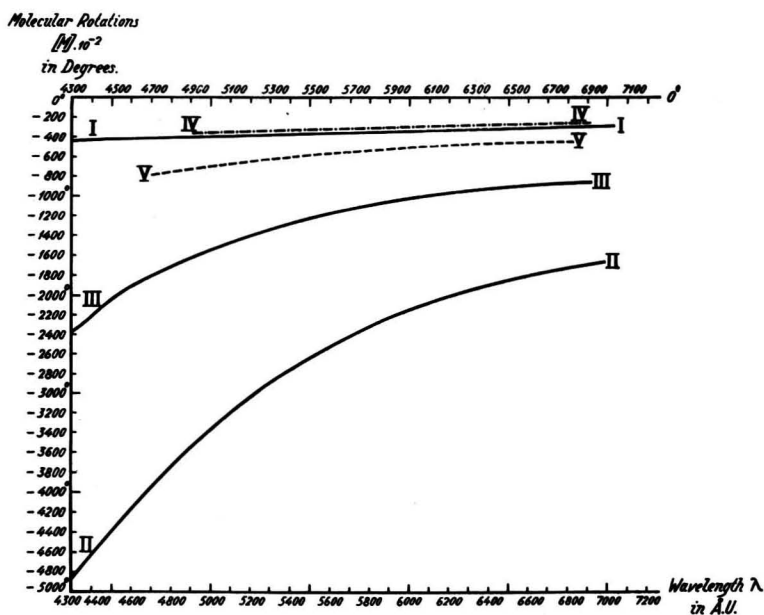


Fig. 4. Rotatory Dispersion of Levogyrotory Triethylenediamine(I), Triclopentanediamine(II), and Trictrichlohexanediamine(III)-Rhodiumchlorides, all isolated from the least-soluble *Cl*- and *Br*-*gl*-Tartrates. IV is the curve for $L\text{-}\{Rh(L\text{-}\beta\text{-}2\text{-}4\text{-}Ptn)\}_3Cl_3$; V that for $L\text{-}\{Rh(\alpha\text{-}meso\text{-}2\text{-}4\text{-}Ptn)\}_3Cl_3$. (Ethylenediamine and $\alpha\text{-}meso\text{-}2\text{-}4\text{-}norm$. Pentanediamine are non-resolvable; the salts of the two resolvable cyclic Diamines have the Constitution: $\{Rh(gl\text{-}Cptn)\}_3Cl_3$ and $\{Rh(gl\text{-}Chen)\}_3Cl_3$ respectively. The curves I, II and III probably have all a flat minimum in the neighbourhood of 3000 Å.U. and evidently show a circular dichroism of negative character.

Fig. 4. Rotatory Dispersion of Different Rhodium-Salts.

configuration as the corresponding *dextrogyrotory cobaltic*-salt. From all these corrolaries it follows, that also in the case of the *tricyclohexanediamine*-salts, the substitution of the central Co-atom by a Rh-atom and *vice-versa* must cause a reversion of the rotation of the complex itself which, in the red part of the spectrum, is only *apparently* hidden by the *levogyrotory* superimposed influence of the 3 *dextrogyrotory* molecules of the base introduced into it. Simultaneously it becomes clear, that here the solubility-rule of WERNER equally holds and that the disagreement mentioned in § 4 is only an *apparent* one, — conjured up, as it were, by the strong *levogyrotory* influence exerted by the three molecules of the *d*-base present in the complex *cobaltic*-ion. The *rhodium*-salt, it is true, has a circular dichroism (in the vicinity of 3000 Å.U.) of *negative* character; but the same occurs in the case of the *levogyrotory triethylenediamine-rhodium*-salt, which equally has the same spatial arrangement as the *dextrogyrotory*

¹⁾ Because it never can rise higher than the curve I, which corresponds to completely *inactive* basic molecules in the complex ion.

cobaltic-compound; and it is, therefore, evidently characteristic of *rhodium*-salts of this type. This negative COTTON-effect is actually co-ordinated with the fact, that all these *rhodium*-salts are *levogyrotory* in the *red* part of the spectrum. Most probably the absorption-band of the *rhodium*-salts in the ultraviolet really corresponds to that of the *cobaltic*-salts at about 4600—5300 A.U.; the *rhodium*-salts themselves are colourless¹⁾).

So far therefore, a perfect agreement exists between the deductions from WERNER's rule and from the other sources of information.

In the following paper we have to consider some facts concerning the *cyclopentanediamine*-salts in connection with the *triethylenediamine*-compounds, which, at first sight, seem to be in partial contradiction with the phenomena here discussed.

SUMMARY.

1. By means of the method of the optically-active racemates the validity of WERNER's solubility-rule was demonstrated as well in the case of the *triethylenediamine*-, as of the *tricyclohexanediamine*-salts of *cobaltum* and *rhodium*. The only apparent disagreement in the case of $L\text{-}\{Co(d\text{-}Chxn)_3\}Cl_3$ was explained as certainly being caused by the superimposed action of the optically-active base present in the complex. The salts isolated from the least-soluble *chloro*- or *bromo-d-tartrates* all possess the spatial configuration characteristic of the *dextrogyrotory triethylenediamine*-ion.

2. As well in the case of the *triethylenediamine*-, as in that of the *tricyclohexanediamine*-salts the substitution of the central Co-atom by a *Rh*-atom not only causes a change of the magnitude, but simultaneously a *reversion* of the algebraic sign of the rotation of the complex, when that substitution occurs in ions with the same absolute spatial configuration.

¹⁾ According to I. LIFSCHITZ and E. ROSENBOHM (Zeits. f. phys. Chem., **97**, 1, (1920); Zeits. f. wiss. Photogr. etc., **19**, 198 (1920)) the *triethylenediamine-cobaltic*-salts have absorptionbands at about 4550 A.U., at 3390 A.U. and in the ultraviolet; those of *rhodium* at about 3000 A.U. and 2600 A.U., but not in the visible part of the spectrum.

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