

Chemistry. — *On the Relative and Absolute Spatial Configuration of Isomorphous, Optically active Complex Salts: II. Comparison of the Tri-diamino-Salts of Cobaltum, Rhodium and Chromium.* By F. M. JAEGER.

(Communicated at the meeting of January 30, 1937).

§ 1. In continuation of our previous considerations ¹⁾ about the spatial configuration of some *tridiamino*-salts of *cobaltum* and *rhodium*, an analogous comparison of the *tricyclopentanediamine*-derivatives of these metals, also including the *chromic* salts of the bases hitherto discussed, will follow in the present paper.

As to the *chromium* salts involved, in general it can be remarked that for their preparation we started from *trichloro-tripyrindine-chromium* :



which, after purification ²⁾, was introduced into the pure, heated bases; the mass thus obtained was carefully heated with a small flame and subsequently on the waterbath for some time, then dissolved in as little tepid water as possible and cooled to room-temperature: in the case of the *cyclopentanediamine*-salt ordinarily the substance is partially deposited in beautiful, yellow or yellowish-orange crystals and the rest is precipitated from the mother-liquor by an excess of absolute alcohol, because heating of the liquid on the waterbath must be avoided, as the *chromic* salt of this base proves to be decomposed under these circumstances with the precipitation of a dark, bluish-violet, initially gelatinous mass.

In the case of the *cyclohexanediamines*, the heating of the $\left\{ \begin{array}{c} (C_5H_5N) \\ Cr \\ Cl_3 \end{array} \right\}$ with the base can safely occur in *absolute* alcohol, from which the complex salts desired, after some time, are readily deposited in the form of a pale yellow powder which can be recrystallized from water without decomposition.

On the other hand, care must be taken *not* to heat the aqueous solution of the *triethylenediamine*-salt, because this, even at room-temperature, is

¹⁾ F. M. JAEGER, These Proceedings, **40**, (1937), p. 3. The notations *D*- and *L*- in this paper have the same meaning as in the previous one and relate to the rotation of the complex ions only in the *red* part of the spectrum.

²⁾ The pure *trichloro-tripyrindine-chromium*-salt used crystallizes in green *monoclinic-prismatic* (pseudo-ditrigonal) crystals with: $a : b : c = 0.737 : 1 : 0.263$; $\beta = 60^\circ 34'$, and the forms: $m = \{110\}$; $c = \{001\}$; $a = \{100\}$; $r = \{503\}$; $p = \{250\}$. They are either tabular parallel to $\{001\}$, or short-prismatic parallel to the *c*-axis. The forms *a*, *r* and *p* are often absent. Optically biaxial; the plane of the axes is $\{010\}$; double refraction positive. Small optical angle, with the 1st bissectrix almost perpendicular to $\{100\}$.

rapidly transformed into a *diaquo*-salt when in contact with water. For this reason the original, highly concentrated aqueous solution is immediately precipitated with an excess of absolute alcohol, etc., and the solutions were always kept in the dark, because the light appreciably accelerates the said transformation. From the final mother-liquors the last quantities of all these salts also can be isolated in the form of the only sparingly soluble iodides.

The *chromic* salts thus obtained prove to be rigorously isomorphous with the corresponding *cobaltic* as well as with the *rhodium*-salts of the three series of compounds and they show the same crystallographic habitus and the same limiting faces.

§ 2. From the *least-soluble halogeno-d-tartrates* the *chlorides* were isolated which, in the case of the *chromium* salts, proved to be: $D\text{-}\{Cr(Ene)_3\}Cl_3 + 1H_2O$; $L\text{-}\{Cr(d-Chxn)_3\}Cl_3 + 3H_2O$ and $L\text{-}\{Cr(d-Cptn)_3\}Cl_3 + 3H_2O$ respectively. In the same way from the *least-soluble chloro-d-tartrates* of the *tricyclopentanediamine-cobaltic*- and *rhodium*-salts, the *chlorides*: $L\text{-}\{Co(d-Cptn)_3\}Cl_3 + 3H_2O$ and $L\text{-}\{Rh(d-Cptn)_3\}Cl_3 + 3H_2O$ were obtained. All these optically active *tricyclopentanediamine* salts crystallize in beautiful hexagonal bipyramids, whilst the racemic salts are triclinic¹⁾. The optically active *triethylenediamine-chromic* salts are tetragonal, the *racemate* ditrigonal; the optically active $\{Cr-(Chxn)_3\}Cl_3 + 3H_2O$ is hexagonal-pyramidal, the corresponding racemic *Cr*-salt ditetragonal. In this respect there exists, therefore, an exact parallelism between the three series of *Co*-, *Cr*- and *Rh*-salts of the same kind. The presence of the *d*-bases in these complex ions was, as usual, demonstrated by the destruction of the salts by means of *KOH* and by subsequent identification of the base thus set free.

§ 3. By means of the method of the optically active racemates the following evidence concerning the relative spatial configurations of these salts was obtained:

1. From a mixed, equimolar solution of $L\text{-}\{Cr(Ene)_3\}Cl_3$ and of $L\text{-}\{Rh(Ene)_3\}Cl_3$ or of the two corresponding *D*-salts, *ditrigonal* crystals of the optically active *racemate* are obtained. On the other hand, $L\text{-}\{Cr(Ene)_3\}Cl_3 + D\text{-}\{Rh(Ene)_3\}Cl_3$ and $L\text{-}\{Cr(Ene)_3\}Cl_3 + L\text{-}\{Co(Ene)_3\}Cl_3$ yield clear, homogeneous *tetragonal mixed crystals*. From this it follows that the *L*-*Cr*-, *L*-*Co*- and *D*-*Rh*-salts of this series have *the same* spatial configurations. Previously²⁾ we emphasized that these ions all correspond to the absolute configuration made probable for the *D*- $\{Co(Ene)_3\}$ -ion.

2. From equimolar mixed solutions of $D\text{-}\{Co(l-Cptn)_3\}Cl_3 + D\text{-}\{Rh(l-Cptn)_3\}Cl_3$ very beautiful *mixed crystals* of *hexagonal* (apparently

¹⁾ Cf. F. M. JAEGER and H. B. BLUMENDAL, *Zeits. f. anorg. Chem.*, **175**, (1928), 192, 208, 209.

²⁾ These Proceedings, **40** (1937), p. 3.

bipyramidal) symmetry were obtained, which completely corresponded to the form of the optically active components. The same occurs with the two *L*-salts mixed. On the other hand, mixed solutions of $D\text{-}\{Co(l\text{-}Cptn)_3\}Cl_3 + L\text{-}\{Rh(d\text{-}Cptn)_3\}Cl_3$ or of $L\text{-}\{Co(d\text{-}Cptn)_3\}Cl_3 + D\text{-}\{Rh(l\text{-}Cptn)_3\}Cl_3$, yield flat *triclinic-pinacoidal* crystals of the active *racemate*; the crystals only *apparently* seem to be monoclinic by a twinning parallel to $\{110\}$, but they have the same angles as the pure *racemates* of this series.

From a solution of an equal number of molecules: $L\text{-}\{Cr(d\text{-}Cptn)_3\}Cl_3 + D\text{-}\{Rh(l\text{-}Cptn)_3\}Cl_3$, on evaporation in the darkness, splendid, *triclinic* crystals of the *racemate* were obtained with the typical angles ¹⁾: $a:m=77^\circ 5'$; $a:p=53^\circ 34'$; $\omega:p=64^\circ 24'$; $p:s=58^\circ 40'$; etc. of the crystals of the pure components. On the contrary, from an analogously constituted, mixed solution of $D\text{-}\{Cr(l\text{-}Cptn)_3\}Cl_3 + D\text{-}\{Rh(l\text{-}Cptn)_3\}Cl_3$ the clear orange or yellow *mixed crystals* of hexagonal symmetry were obtained, as are typical for the free optically active components.

As a controlling experiment, the latter fact was also proved for a mixture of the *D*-salts of *chromium* and of *cobaltum*.

From these facts it becomes clear that beyond any doubt the *D*-*Cr*-, *D*-*Co*- and *D*-*Rh*-salts of this series all have *identical* spatial configurations and, therefore, the same is true for all *L*-salts of the three metals.

3. From equimolar mixed solutions of $L\text{-}\{Co(d\text{-}Chxn)_3\}Br_3 + L\text{-}\{Rh(d\text{-}Chxn)_3\}Br_3$, as we previously demonstrated, clear, typically hemimorphous *hexagonal-pyramidal mixed crystals* were obtained. The same proved to be true for $D\text{-}\{Cr(l\text{-}Chxn)_3\}Cl_3 + D\text{-}\{Rh(l\text{-}Chxn)_3\}Cl_3$ and for $L\text{-}\{Cr(d\text{-}Chxn)_3\}Cl_3 + L\text{-}\{Rh(d\text{-}Chxn)_3\}Cl_3$: optically uniaxial, negative crystals were formed with $\{10\bar{1}1\}$, $\{0001\}$ small, $\{000\bar{1}\}$ large and the typical angular values of the pure components. From the mixtures of the *L*- + *D*-salts, on the other hand, the long, *ditetragonal* needles or prisms of the *racemate* were obtained. Mixed solutions of the *D*-*Co*- + *D*-*Cr*-salts and reversibly, yielded clear *mixed crystals* of the components; those of *D*-*Co*- + *L*-*Cr*-salts, etc. the *ditetragonal* crystals of the *racemate*.

Therefore, the *D*-salts of the three metals and equally so the *L*-salts undoubtedly all possess *the same* spatial configurations and the mutual relations between them are the same as in the case of the *tricyclopentane-diamine* salts mentioned above.

In connection with the results obtained from the solubility-experiments with the *halogeno-d-tartrates*, it appears, therefore, that all ions corresponding to the *least-soluble halogeno-d-tartrates* really possess the spatial configuration of the $D\text{-}\{Co(Ene)_3\}^{***}$ -ion: the results obtained by the two methods used are in full agreement with each other.

§ 4. The *rotatory dispersion* of these salts of *cobaltum*, *chromium* and *rhodium*, however, does *not* show the same congruency in its character, — as may be seen from the following tables and from the figures 1 and 2.

The *rotatory dispersion* of the *chlorides* of the *tricyclopentanediamine*-

cobaltic and rhodium salts, isolated from the least-soluble chloro-*d*-tartrates, is known¹⁾ and is, for the cobaltic salt, graphically represented in Fig. 1. The two salts are levogyrotory for all wave-lengths in the interval of the spectrum considered and they have the constitution: $L\text{-}\{\text{Co}(d\text{-Cptn})_3\}\text{Cl}_3 + 3\text{H}_2\text{O}$ and $L\text{-}\{\text{Rh}(d\text{-Cptn})_3\}\text{Cl}_3 + 3\text{H}_2\text{O}$ respectively.

The corresponding data for $L\text{-}\{\text{Cr}(d\text{-Chxn})_3\}\text{Cl} + 3\text{H}_2\text{O}$ and for $L\text{-}\{\text{Cr}(d\text{-Cptn})_3\}\text{Cl}_3 + 3\text{H}_2\text{O}$ are given in table I, II and in Fig. 2.²⁾

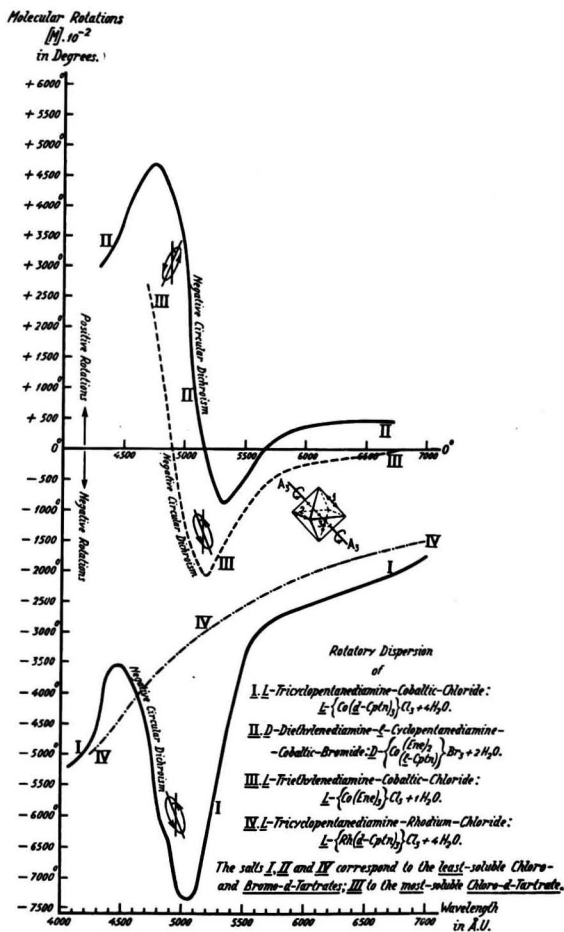


Fig. 1. Rotatory Dispersion of the Complex Co- and Rh-Salts.

From these data and graphs now it is immediately evident that in the case of the tricyclohexane-, as well as in that of the tricyclopentanediamine-salts the cobaltic and the chromic salts behave just in the same way. The tricyclohexanediamine-chromic-chloride shows a curve for its rotatory

¹⁾ F. M. JAEGER and H. B. BLUMENDAL, Zeits. f. anorg. Chem., **175**, (1928), 201, 203, 217.

²⁾ According to I. LIFSCHITZ and E. ROSENBOHM (Zeits. f. wiss. Photographie, etc. **19**, 204 (1920), the $\{\text{Cr}(\text{Ene})_3\}$ -ion shows absorption-bands at about 4610, 3570 and 2700 A.U. respectively.

TABLE I.
Rotatory Dispersion of $L\text{-}\{Cr(d\text{-}Chxn)_3\}Cl_3 + 3H_2O$.

Wave-lengths λ in Å.U.:	Specific Rotation $[\alpha]$:	Molecular Rotation $[M]$. 10^{-2} :
6980	— 60°	— 300°
6730	— 60	— 300
6480	— 58	— 290
6262	— 48	— 240
6074	— 35	— 175
5893	— 25	— 125
5735	— 4	— 20
5592	+ 28	+ 140
5463	+ 85	+ 425
5340	+ 180	+ 900
5224	+ 252	+1260
5126	+ 370	+1850
5036	+ 450	+2250
4950	+ 390	+1950
4861	+ 325	+1625
4793	+ 180	+ 900
4724	— 360	—1800
4690	— 490	—2450
4596	—1070	—5350

Concentrations of the solution: 0.50 0/0, 0.20 0/0 and 0.08 0/0.

dispersion which is quite analogous to that of the corresponding *tricyclohexanediamine-cobaltic* salt¹⁾; and for the same reasons as previously exposed, this curve for the *chromic* salt is only *apparently* an exception to the suggestions made by KUHN and BEIN²⁾ concerning the relations between the character of the dispersion and the circular dichroism on the one hand and of the absolute spatial configuration of the complex ion on the other: in reality it may be considered to be in agreement with the rotatory dispersion and the circular dichroism of an ion having the architecture of the $D\text{-}\{Co(Ene)_3\}^{3+}$ -ion.

In the case of the *tricyclopentanediamine* salts, the *Co*- and *Cr*-

1) These Proceedings, 40, (1937), p. 3; fig. 3.

2) Ibidem, p. 3.

TABLE II.
Rotatory Dispersion of $L\text{-}\{Cr(d\text{-}Cptn)_3\}Cl_3 + 3H_2O$.

Wave-length λ in Å.U.:	Specific Rotation $[\alpha]$:	Molecular Rotation $[M]$: 10^{-2} :
6980	— 155.2	— 795°
6730	— 161.9	— 830
6480	— 182.4	— 935
6262	— 191.2	— 980
6074	— 199.0	—1020
5893	— 202.9	—1040
5735	— 189.3	— 970
5592	— 185.4	— 950
5463	— 142.4	— 730
5340	— 126.8	— 650
5224	— 109.3	— 560
5126	— 206.8	—1060
5036	— 320.0	—1640
4950	— 565.9	—2900
4861	—1166.8	—5980
4793	—1239	—6350
4724	—1079	—5530
4658	— 983	—5038
4596	—1190	—6098
4537	—1153	—5910
4483	— 946	—4848
4430	— 687	—3523
4380	— 481	—2462
4335	— 392	—2008

Concentrations of the solution: 0.1352 % and 0.20 %.

compounds equally show a similar behaviour in so far *that they both manifest the same abnormality*: although the two ions, according to our previous experiments, have the same absolute spatial configuration as the $D\text{-}\{Co(En)_3\}^{+++}$ -ion, yet they both prove to be *levogyrotory* for *all* wave-lengths between 4200 and 7000 Å.U., — the interval within which their

first absorption-band with respect to the red part of the spectrum is situated.

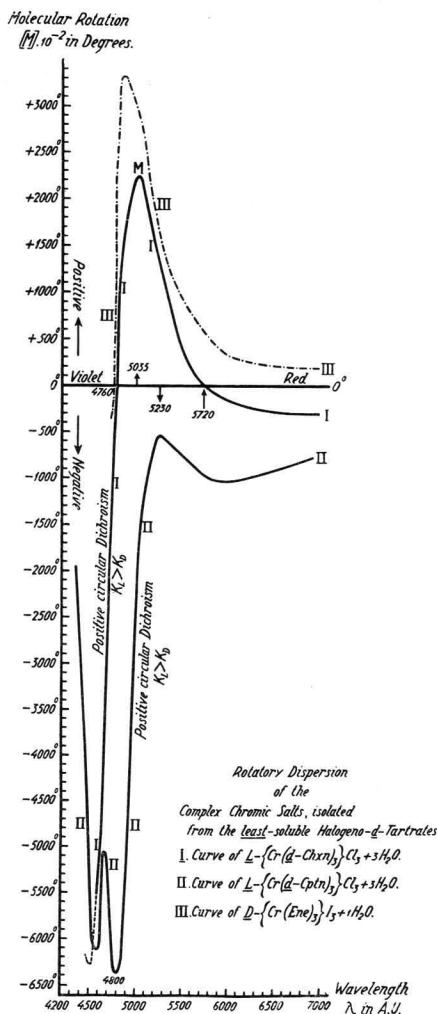


Fig. 2. Rotatory Dispersion of the Complex Chromic Salts.

In the case of the chromium-compound, however, the similarity of the dispersion-curve with that characteristic of the $D\text{-}\{Co(Ene)_3\}^{3+}$ -ion, — although much feebler than in the case of the tricyclo-hexanediamine derivatives, — can still be recognized: the maximum at about 5200 A.U. and the positive COTTON-effect within that band really stamp this curve as still being in a principal agreement with the character of the dispersion-curve of $D\text{-}\{Co(Ene)_3\}Cl_3$.

But in the case of the cobaltic salt (Fig. 2) even this feeble similarity proves to have completely disappeared: here the whole character of the curve, with its negative COTTON-effect, has unmistakably become that of the enantiomorphous salt: $L\text{-}\{Co(Ene)_3\}Cl_3$ and has got the same type as met with in the case of the levogyrotory rhodium salts. It makes the

impression as if the central Co-atom here suddenly starts to play the role of a "modified *Rh*-atom" within a complex ion with the same absolute spatial configuration as the $D\text{-}\{Co(Ene)_3\}^{\dots}$ -ion has (Table III, c).

This fact is quite contradictory to the connections which, according to KUHN and BEIN, should exist between the absolute spatial arrangement of the complex ions of this type and the characteristic optical behaviour of those ions: it demonstrates, indeed, that the relations supposed by them have by no means such a general validity as they believe and certainly do not furnish such reliable indications for establishing the similarity in the spatial structure of these relatively simply constituted, optically active substances as the two methods first discussed really prove to yield. As the somewhat more reddish colour of the *cobaltic* salt of *cyclopentanediamine* already

TABLE III.
REVIEW
of the Determined spatial Configurations of the Complex Tridiamino-Ions of trivalent Cobaltum, Chromium and Rhodium

a) After the Method of corresponding Solubilities: (corr. to the <i>least-soluble Halogeno-d-Tartrates</i>)		b) After the Method of the active Racemates:		c) Apparent absolute Configuration according to the Rotatory Dispersion and the Circular Dichroism:	
Series:	Configuration:	Configuration:	Crystallographic Symmetry:	Kind of rotatory Dispersion:	Algebr. Sign of COTTON-Effect:
I.	$D\text{-}\{Co(Ene)_3\}^{\dots}$ $D\text{-}\{Cr(Ene)_3\}^{\dots}$ $L\text{-}\{Rh(Ene)_3\}^{\dots}$	$D\text{-}\{Co(Ene)_3\}^{\dots}$ $D\text{-}\{Cr(Ene)_3\}^{\dots}$ $L\text{-}\{Rh(Ene)_3\}^{\dots}$	Tetragonal Racem.: Ditrigonal	$D\text{-}Co(Ene)_3$ Scheme <i>idem</i> <i>idem</i>	+ + -
II.	$L\text{-}\{Co(d-Cptn)_3\}^{\dots}$ $L\text{-}\{Cr(d-Cptn)_3\}^{\dots}$ $L\text{-}\{Rh(d-Cptn)_3\}^{\dots}$	$L\text{-}\{Co(d-Cptn)_3\}^{\dots}$ $L\text{-}\{Cr(d-Cptn)_3\}^{\dots}$ $L\text{-}\{Rh(d-Cptn)_3\}^{\dots}$	Hexagonal Racem.: Triclinic	$L\text{-}Co(Ene)_3$ Scheme $D\text{-}Co(Ene)_3$ Scheme <i>idem</i>	- + -
III.	$L\text{-}\{Co(d-Chxn)_3\}^{\dots}$ $L\text{-}\{Cr(d-Chxn)_3\}^{\dots}$ $L\text{-}\{Rh(d-Chxn)_3\}^{\dots}$	$L\text{-}\{Co(d-Chxn)_3\}^{\dots}$ $L\text{-}\{Cr(d-Chxn)_3\}^{\dots}$ $L\text{-}\{Rh(d-Chxn)_3\}^{\dots}$	Hexagonal Racem.: Ditetragonal	$D\text{-}CoEne_3$ Scheme <i>idem</i> <i>idem</i>	+ + -

betrays, — the absorption of this salt, starting already in the *middle* part of the green rays, is certainly somewhat different from that of the other *tridiamino*-salts of *cobaltum*; but considering the further complete similarity in all the other physical properties of this *cobaltic* salt (analysis; crystal-form; isomorphism) with those of the analogous *chromium* and *rhodium* salts, — this fact can by no means be the true cause of the curious phenomenon, that its rotatory dispersion suddenly changes into exactly the *opposite* character of what should be expected. Neither can it at present be explained *what* special property of this base, with its *flat* cycle of C-atoms, may be the real cause of the deviating behaviour of its complex *cobaltic* salt and *why* that property then does not simultaneously manifest itself also in the case of the corresponding *rhodium*-, and only rather feebly in that of the *chromic* ion.

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Chemistry. — *Investigations on the Complex Salts of the Racemic and Optically active Cyclohexanediamines with trivalent Cobaltum and Rhodium. II. The Complex Tricyclohexanediamine-Rhodium-salts.* By F. M. JAEGER and L. BIJKERK.

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§ 1. The inactive base as well as the optically active components¹⁾ of it can, of course, be used in the preparation of the complex *rhodium* salts. In the former case the thus obtained racemic salts can subsequently be resolved into the optically active antipodes and the latter then be compared with the products obtained by direct synthesis, when starting from the optically active bases.

In this way their true constitution can be ascertained, which afterwards can again be controlled by destruction of the salts by means of caustic potash and sodium formiate and by the subsequent setting free of the active base contained in them.

Exactly as in the case of the corresponding *cyclopentanediamine*-derivates²⁾ it was observed here that the reactions in which the complex salts were generated from the optically active *diamines* and from optically inactive compounds, like for instance *sodium-rhodium-chloride*, always are

¹⁾ F. M. JAEGER and L. BIJKERK, Proc. Royal Acad. Amsterdam, **40**, 12 (1937).

²⁾ F. M. JAEGER and H. B. BLUMENDAL, Zeits. f. anorg. Chemie, **175**, 165 (1928).