Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

**Chemistry.** — *Investigations into* Pasteur's *Principle of the Connection between Molecular and Crystallonomical Dissymmetry:* **IV.** *Racemic and Optically-active Complex Salts of Rhodium-tri-oxalic Acid.* By Prof. Dr. F. M. Jaeger.

§ 1. In our previous papers we had occasion to draw attention to the fact that the crystals of the optically active components which, according to Werner's theory, may be obtained under definite circumstances from the racemic complex salts of the general type: $\{Me\,X''_3\}\,Y_n$, exhibit occasionally the non-superposable hemihedrism to be expected according to Pasteur's principle, but that in other cases of this kind no evidence whatever of this hemihedrism is detectable by any experimental method at hand.

At the same time attention was drawn to the other fact that the molecular dissymmetry in cases as these, is by no means caused by a total absence of symmetry-properties in the molecule, but that the complex ions of the type mentioned, if once Werner's theory be adopted, must possess a configuration of their radicals in space, possessing the symmetry of the *trigonal-trapezohedral* class $(D_3)$. From the established fact that the *non*-superposable hemihedrism of the crystal-forms could not be stated in several cases where derivatives of the complex *tri-ethylenediamine-cobalti*-ion $\{Co(Eine)_3\}\cdots$ were. studied, we were compelled to conclude that the cause of this abnormal behaviour must be ascribed to the particular circumstance that the radicals placed round the central metal-atom are chemically identical here. It was remarked, however, that the expected hemidedrism could be stated *without exception in all cases*, where in the salts investigated radicals containing oxygen [1]) were present.

It was of interest to study other instances of this kind. Thus such analogously composed salts were chosen in the first place, as contained the oxygen-bearing radicals immediately linked to the central-atom in the form of the radicals of bivalent carboxylic acids. Our choice was finally fixed upon salts derived from the complex

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1) F. M. Jaeger, Proceed. Kon. Acad. Amsterdam, 17. 1217. (1915); 18. 49. (1915); Zeits. f. Kryst. u. Min. 55. 209. (1915). .

*rhodium-tri-oxalic acid*, for which the possibility of a fission into the optically-active components had been proved experimentally [1]. Moreover, a detailed investigation of these salts appeared also desirable from another point of view, because in WERNER's original paper some facts are mentioned concerning the crystallisation-phenomena of the optically-active components, which à priori must be considered very improbable, and therefore worth controlling again by means of new experiments.

For instance, the fact was there brought to the fore, that from solutions of the racemic compound under favourable conditions crystals of both the enantiomorphous modifications would be deposited spontaneously, which hemihedral crystals of the optically active components, if brought at room-temperature into a concentrated solution of the racemoid, would increase slowly and grow to big individuals within a few weeks. But, as we found during our investigations, that the optically active forms are much more soluble under the same circumstances than the racemic substance is, it seemed highly probable that an error was made here, because, moreover, the facts mentioned cannot be right from a theoretical standpoint. The drawings in WERNER's paper, intended to give an impression of the crystal-forms obtained, rather point to distorted, and accidentally non-superposable *triclinic* crystals of the racemoid being present here, than to enantiomorphous crystals of true hemihedral symmetry. Moreover, WERNER himself mentions the *triclinic* symmetry of these crystals, and therefore the validity of PASTEUR's principle in his case cannot yet be considered as proved by the data given in this paper. Repeatedly we have made attempts in the way indicated by WERNER, to perform a spontaneous fission of the racemic salt; but the solution of it saturated just above 100° C., first being rapidly cooled down to 90° C., and subsequently cooled down to room-temperature, never deposited other crystals than the capriciously distorted individuals of the triclinic racemoid. The microscopically small crystals often obtained by very rapid cooling of the hot solution, appeared to be no crystals of the active forms either; they were rhombic individuals exhibiting prismatic, domatic and basal facets, of a new hydrate of the racemic compound, probably at higher temperatures stable, and containing less water of crystallisation. These experiments, if varied in several ways, gave unexceptionally bigger or smaller crystals of the racemic compound. The appreciably greater solubility of the active forms in comparison with that of

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[1] A. WERNER, Ber. d. d. Chem. Ges. **47**. 1954. (1914).

the racemic salt at all temperatures between 15° and 100° C. characterizes the racemoid undoubtedly as the more stable solid phase within this range of temperature, with respect to the mixture of these antipodes. The experiment described by WERNER can therefore *never* lead to a spontaneous fission, and surely it must be quite impossible, that under these conditions an optically active crystal should increase, when brought at room-temperature into the saturated solution of the racemic salt. This may readily be deduced from BAKHUIS ROOZEBOOM's well-known graphical representations [1]) of the solubility-relations here prevailing. Indeed, it could be proved on the contrary by often repeated experiments, that a crystal of one of the optically-active forms, if brought into a feebly supersaturated or saturated solution of the racemic salt, *immediately disintegrates and subsequently disappears completely*, and that after some lapse of time, *triclinic* crystals of the racemic compound are deposited from the solution. These last crystals are often rudimentarily developed, so that occasionally they make the impression of *pedial*, unsymmetrical crystals, which of course must therefore appear non-superposable with their mirror-images. If dissolved in water, the solutions of these crystals were in every case optically *inactive*, There can be no doubt whatever therefore about the fact, that the crystals obtained and reproduced by WERNER must have been distorted triclinic crystals of the racemic salt; it remains, however, doubtful whether the solutions obtained by him in dissolving these crystals, can really have been "optically-active", unless some optically-active crystals for inoculation-purposes were previously introduced into the solutions.

We were able, moreover, to demonstrate the remarkable fact that the crystals of the pure optically active components exhibit exactly the same symmetry as that previously deduced for the complex ions of this type themselves. Indeed, they are *trigonal-trapezohedral*, and they show forms which externally are quite comparable with the typical forms of some dextro- or laevogyratory *quartz*-crystals.

The racemic salt was prepared from freshly precipitated and washed *rhodium-hydroxide* obtained from *sodium-rhodium-chloride* by means of a dilute *sodium hydroxide*-solution at 40° C.; the pure *rhodium-hydroxide* was then dissolved in a hot solution of *potassium-bi-oxalate*. The fission into its components, which is a rather tedious process, was executed by means of the *strychnine*-salt, from which afterwards the *strychnine* was readily eliminated in the form of its *iodide*.

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[1]) H. W. BAKHUIS ROOZEBOOM, Zeits f. phys. Chemie, **28**. 494. (1899).

'§ 2. A solution of the active components containing 3,79% of the anhydrous salt, exhibits in a layer of 10 cm. an absorption-spectrum, in which all violet, blue, and green rays are lacking, while of the yellow light only a small portion is transmitted. With increasing dilution a small extension of the spectrum is stated; more particularly the yellow and green rays are gradually better transmitted and become more and more visible. In the case of a solution of 0,5% even some greenish-blue rays were visible. In a layer of 20 cm., the limits between which the light was not appreciably absorbed, appeared to be about as follows:

| Concentration of the solution in percentages of anhydrous salt: | Limits of the transmitted light (in A.U.) for a layer of 20 c.m. |
|---|---|
| 10.96 | 7000—5800 |
| 3.79 | 7000—5700 |
| 2.75 | 7000—5500 |
| 1.97 | 7000—5500 |
| 1.09 | 7000—5100 |
| 0.55 | '7000—4900 |
| 0.50 | 7000—4800 |

These data may give an approximate impression of the extension of the light-transmission for several wave-lengths. In the red part of the spectrum, the limit is situated at about 7700 A U.; however it could not be fixed any more, because of the micrometer-screw of the monochromator not going so far.

By the study of the seven solutions just mentioned, the rotation for any of these wave-lengths was measured in a way analogous to that previously described [1]. The total behaviour of these orange-red to orange-yellow coloured solutions is most remarkable. For instance, if only sufficiently concentrated solutions of the *right*-handed salt be investigated (e.g. of 10%), and thus only a limited spectral region be taken into account, the observer would readily come to the conclusion, that his salt is *laevo*gyratory. The following data, obtained within several spectral regions, by means of the seven solutions mentioned, and which appeared, after controlling, to be sufficiently exact, may elucidate this strange behaviour [2] with the simultaneous

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[1] F. M. JAEGER, Proceed. Kon. Acad. Amsterdam **17**. 1227 (1915).

[2] A. WERNER, loc. cit. 1955.

of fig. 1. The numbers given for the specific rotation $[\alpha]$, are mean values of commonly three or four different values obtained various series of measurements; they always relate to a content anhydrous salt in 100 weight-parts of the solution:

**Rotation-Dispersion of dextrogyrate Potassium-Rhodium-oxalate.**

| Wave-length in ANGSTRÖM-Units: | Specific rotation in Degrees: | Molecular rotation in Degrees: |
|---|---|---|
| 4860 | $+ 356°$ | $+ 17240$ |
| 4950 | $+ 293$ | $+ 14190$ |
| 5020 | $+ 253$ | $+ 12250$ |
| 5100 | $+ 206$ | $+ 9975$ |
| 5180 | $+ 172,1$ | $+ 8335$ |
| 5260 | $+ 141,7$ | $+ 6860$ |
| 5340 | $+ 114,3$ | $+ 5535$ |
| 5420 | $+ 85$ | $+ 4115$ |
| 5510 | $+ 67,1$ | $+ 3250$ |
| 5605 | $+ 46,4$ | $+ 2250$ |
| 5700 | $+ 30,1$ | $+ 1460$ |
| 5800 | $+ 16,3$ | $+ 790$ |
| 5890 | $+ 6,2$ | $+ 300$ |
| 5900 | $+ 5,1$ | $+ 247$ |
| 5970 | $0$ | $0$ |
| 6030 | $- 4,5$ | $- 218$ |
| 6140 | $- 11,5$ | $- 557$ |
| 6260 | $- 17$ | $- 823$ |
| 6380 | $- 21$ | $- 1017$ |
| 6520 | $- 23,5$ | $- 1140$ |
| 6660 | $- 25,1$ | $- 1215$ |
| 6800 | $- 26$ | $- 1260$ |
| 6945 | $- 27,4$ | $- 1330$ |

'rom this it becomes evident that the solutions of the right-handed are only dextrogyratory in reality, if green and yellow light-

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rays be taken into account, for the red and orange rays however, these solutions appear to be laevogyrate.

Such solutions are optically-*inactive* for a wave-length of ·5970 A. U. At this wave-length, invariable moreover for solutions of widely different· concentrations, there is no longer any detectable difference between solutions of the two antipodes.
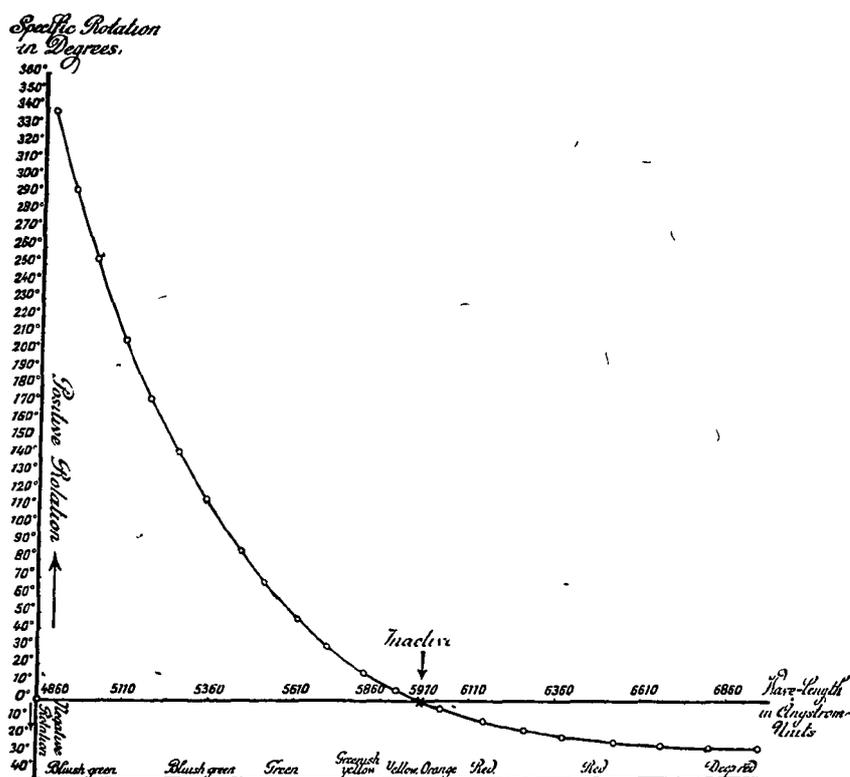


Fig 1.

Specific Rotation-dispersion of right-handed Potassium-Rhodium-Oxalate.
(All molecular rotations are 50 times as great).

It is worth attention, that the solutions do *not* exhibit for this wave-length any trace of an absorption-line. Our former supposition connecting the abnormal rotation-dispersion with the eventual occurrence of selective absorption, thus appears *no* longer justified. As WERNER points out, the phenomenon is met with in the study of all complex metal-oxalates hitherto investigated: those of *rhodium*, *chromium*, and *cobaltum*, exhibit this property in a very pronounced way[1].

[1] To an investigator studying the heterogeneous equilibria between the racemic salt and both its antipodes in solution, there could no longer be any difference between the solutions of the d- and l-component or their mixtures, if he worked under conditions which enabled him only to use light of a wave-length of $\lambda = 5970$ A.U. Indeed, all such solutions would then be found optically *inactive*. In such circum-

Finally it may be remarked, that the optically-active salts have no appreciable tendency to auto-racemisation. After heating on the water-bath during some time, no appreciable diminution of the original rotatory power appears to have occurred. A slight hydrolysation, however, could be stated in these cases. The salts are slowly decomposed by the continued action of violet light or by strong heating, while a black powder (*Rho* ?), and some *rhodium-hydroxide* are set free.

§ 3. I. Racemic Potassium-Rhodium-Oxalate (+ 4½ H$_2$O).

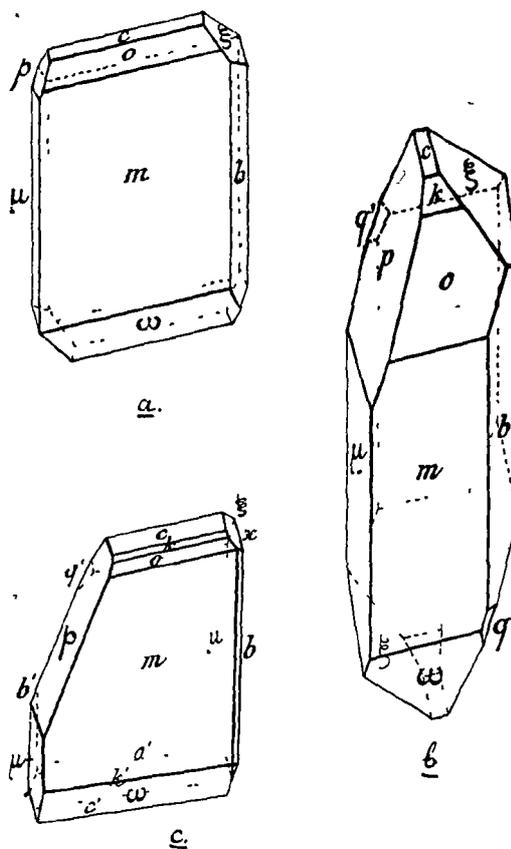This compound crystallizes in big, ordinarily flattened, garnet-red,



Fig. 2.

Racemic Potassium-Rhodium-Oxalate (+ 4¹/₃ H$_2$O).

stances no difference would apparently be any longer present here and in the well-known case of *sodium-chlorate*; in other words: in this singular point the descriptive number of components would be diminished with one. However, it must be insisted, that this is only valid for one definite temperature and one definite pressure, as ⌊z⌋ is a function of both. For wave lengths only slightly smaller or greater than 5970 A.U., the system is again a *ternary* one, in which the functions of *d*- and *l*-components are reversed.

very lustrous, and perfectly transparent crystals. Their shape is very variable, and some of the most frequent forms are reproduced in fig. 2 $a-c$. The external aspect is often highly unsymmetrical (fig. 2c); in such cases individuals are occasionally met with, which may be looked upon as apparently enantiomorphous. However, their symmetry is most probably holohedral, the present forms therefore only being special and accidental forms of growth.

The crystals are identical with those studied by DUFET [1]; they differ from those only in aspect, as DUFET's crystals exhibited the form $\mu = \{1\bar{1}0\}$ predominant.

### Triclinic - pinacoidal.

$$a : b : c = 1{,}0732 : 1 : 1{,}0316.$$

| | |
|---|---|
| $A = 92°45\frac{1}{2}'$ | $\alpha = 98°10\frac{2}{3}'$ |
| $B = 102\ \ 4\frac{1}{3}$ | $\beta = 104\ 17\frac{1}{3}$ |
| $C = 67\ 24\frac{1}{2}$ | $\gamma = 66\ 11\frac{2}{3}$ |

*Forms observed*: $m = \{110\}$, very lustrous and predominant; $\mu = \{1\bar{1}0\}$, smaller, but also well reflecting; $b = \{010\}$, commonly a little broader than $\mu$; $\omega = \{11\bar{1}\}$, broad and yielding good reflexes; $\xi = \{1\bar{1}2\}$, well developed and very lustrous; $p = \{1\bar{1}1\}$, commonly smaller, but rarely also much greater than $\xi$, and giving eminent reflexes; $c = \{001\}$, commonly very narrow, occasionally somewhat broader; $o = \{111\}$, broad and beautifully reflecting; $x = \{\bar{1}11\}$, small and lustrous, often absent; $k = \{112\}$, commonly absent, occasionally very narrow, rarely broad; $q = \{02\bar{1}\}$, very small, but well measurable.

| Angles: | | Observed: | Calculated: |
|---|---|---|---|
| $m : b$ | $= (110) : (010) = *$ | 54° 10′ | — |
| $m : \mu$ | $= (110) : (1\bar{1}0) = *$ | 93 3 | — |
| $m : \omega$ | $= (110) : (11\bar{1}) = *$ | 45 24½ | – |
| $b : \omega$ | $= (010) : (11\bar{1}) = *$ | 61 48 | — |
| $\mu : \omega$ | $= (1\bar{1}0) : (11\bar{1}) = *$ | 96 34½ | — |
| $c \cdot b$ | $= (001) : (010) =$ | 87 15 | 87° 14½′ |
| $b' : \mu$ | $= (0\bar{1}0) : (1\bar{1}0) =$ | 32 45 | 32 45½ |
| $m : p$ | $= (110) : (1\bar{1}1) =$ | 86 18 | 86 23 |
| $\omega : c'$ | $= (11\bar{1}) : (00\bar{1}) =$ | 57 50½ | 57 40 |
| $m : \xi$ | $= (110) : (\bar{1}12) =$ | 77 33 | 77 35 |
| $c : \mu$ | $= (00\bar{1}) : (1\bar{1}0) =$ | 95 11 | 95 19 |
| $\mu : \xi$ | $= (1\bar{1}0) : (\bar{1}15) =$ | 51 20 | 51 24 |
| $o : c$ | $= (111) : (001) =$ | 42 14 | 42 14 |
| $m : o$ | $= (110) : (111) =$ | 34 31 | 34 35 |

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[1] H. DUFET, Bull. de la Soc. Min. **12.** 466. (1889); Cf.: E. LEIDIÉ, Ann. de Chim. et Phys (6). **17.** 307. (1889).

| | | Observed: | | Calculated | |
|---|---|---|---|---|---|
| $b':\xi$ | $=(0\bar{1}0) : (1\bar{1}2)=$ | 51 | 25 | 51 | 25 |
| ω $\xi$ | $=(11\bar{1}) : (1\bar{1}2)=$ | 70 | 8 | 70 | 7 |
| $\xi:x$ | $=(\bar{1}\bar{1}2) : (\bar{1}11)=$ | 20 | 47 | 20 | 45 |
| $x:\nu'$ | $=(\bar{1}\bar{1}1) : (\bar{1}10)=$ | 30 | 40 | 30 | 40 |
| $\nu:o'$ | $=(1\bar{1}0) : (\bar{1}11)=$ | 88 | 59 | 89 | 1 |
| $b:o$ | $=(010) : (111)=$ | 64 | 19 | 64 | 24 |
| $o:p$ | $=(111) : (168)=$ | 11 | 35 | 68 | 38 |
| $\nu:p$ | $=(1\bar{1}0) : (1\bar{1}1)=$ | 27 | 58 | 28 | 4 |
| $c':\xi$ | $=(00\bar{1}) \cdot (1\bar{1}2)=$ | 43 | 59 | 43 | 55 |
| $c:p$ | $=(001) : (1\bar{1}1)=$ | 57 | 4 | 57 | 10 |
| $c:k$ | $=(001) : (112)=$ | 27 | 4 | 26 | 56 |
| $k:o$ | $=(112) . (111)=$ | 15 | 10 | 15 | 18 |
| $b:k$ | $=(010) : (112)=$ | 714 | 3 | 71 | 56 |
| $b:q$ | $=(010) : (02\bar{1})=$ | 25 | 4 | 25 | $3\frac{1}{2}$ |
| $c':q$ | $=(00\bar{1}) : (02\bar{1})=$ | 67 | $41\frac{1}{2}$ | 67 | 42 |

No distinct cleavability was found.

The crystals are dichroitic: on {110} for vibrations including an angle of 60° with the edge $m:\mu$ they are orange-yellow; for such perpendicular to those, reddish-orange. On {110} one of the directions of extinction includes an angle of 31° with the intersection $m:\mu$; the plane of the optical axes is almost parallel to the edge $\omega:m$.

§ 4. After transformation of the racemic salt into the corresponding strychnine-salt und fractional crystallisation, the oxalate was resolved into its antipodes. The d-rhodium-salt, namely, combines into a less soluble strychnine-salt than the l-salt does. By treatment with potassium-iodide, all strychnine may be eliminated as the little soluble strychnine-iodide, and in this way the optically active potassium-salts may be obtained. It is a tedious task to get a sufficient quantity of the laevogyrate antipode, because always some strychnine-d-oxalate is withdrawn with the l-oxalate; therefore the last mother-liquids always deposit the racemic salt besides the laevogyrate. Moreover, the result is also diminished by the hydrolysis of the strychnine-salt during the concentration of the mother-liquid on the water-bath.

Finally, however, sufficient quantities of both antipodes were obtained. The crystallographical description of these salts is given in the following paragraphs.

§ 5. II. Dextrogyratory Potassium Rhodium-Oxalate ($+ 1H_2O$).

Splendid, sometimes colossal, very lustrous, blood-red and perfectly transparent crystals. Their external aspect is very variable with the

particular circumstances of crystallisation. and as a consequence of their numerous and most capricious distortions, the right interpretation of the measurements is often very troublesome, Some of the most frequently occurring forms are reproduced in fig. 3 $a$ and $b$.
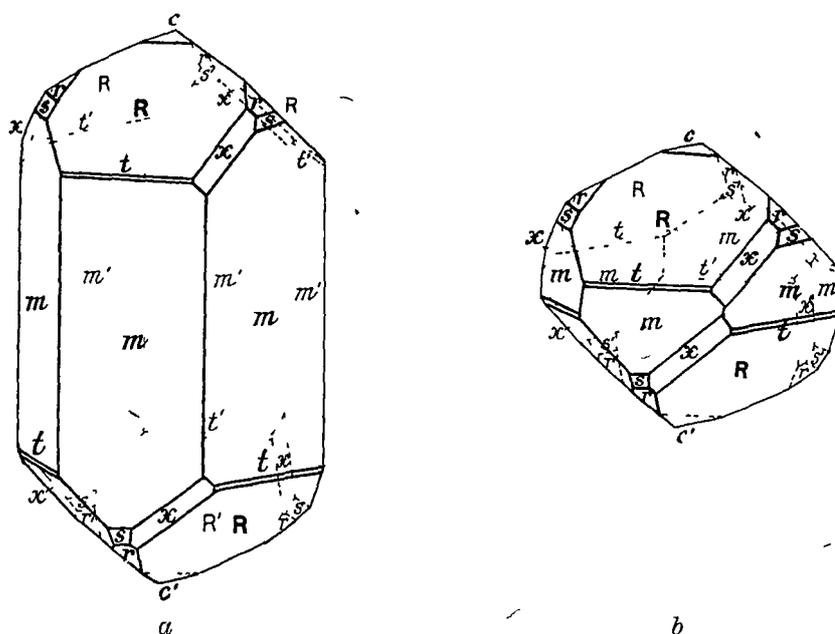


Fig. 3.

Dextrogyrate Potassium-Rhodium Oxalate ($+1$ $H_2O$).

*Trigonal-trapezohedral.*

$$a \cdot c = 1 : 0{,}8938 \text{ (Bravais)}; \quad \alpha = 100°38' \text{ (Miller)}.$$

*Forms observed.* [1]) $R = \{10\overline{1}1\}$ [100], always present, and exhibiting large faces; $c = \{0001\}$ [111], always present too, sometimes very small, but in most cases rather large, $r = \{01\overline{1}1\}$ [221], and $s = \{02\overline{2}1\}$ [11$\overline{1}$], rarely failing, well reflecting, but much smaller than $R$; $t = [20\overline{2}1]$ [5$\overline{1}$1], often absent, always narrow and dull, $m = \{10\overline{1}0\}$ [2$\overline{1}$1], always present, occasionally with small, mostly with well-developed faces, and rarely predominant, $x = \{22\overline{4}1\}$ [71$\overline{5}$], as a right-handed, positive, trigonal bipyramid, occasionally absent, but in several cases with faces almost $^1/_2$ or $^1/_3$ of those of $R$. The different faces of $x$ are in all cases of very different sizes. The aspect of the crystals is occasionally like that of *quartz* (fig. 3$a$), and appreciably distorted; sometimes $t$ is a little broader, so that the external shape gets a more *hexagonal* form. No distinct cleavage

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[1]) The symbols between [ ] are MILLERIAN symbols, relating to the polar edges of $R$ as axes of reference.

was found. On $\{10\bar{1}0\}$ occasionally unsymmetrical corrosion-figures, like trapezia, are observed.

| Angles: | | Observed: | Calculated: |
|---|---|---|---|
| $R:R = (\bar{1}101):(10\bar{1}1) =^*$ | | 76°55′ | — |
| $c:R = (0001):(10\bar{1}1) =$ | | 45 59 | 45°54¼′ |
| $c:r = (0001):(01\bar{1}1) =$ | | 45 58 | 45 54¼ |
| $r:s = (01\bar{1}1):(02\bar{2}1) =$ | | 18 25 | 18 15 |
| $s:m = (02\bar{2}1):(01\bar{1}0) =$ | | 25 31 | 25 51 |
| $m \cdot R = (01\bar{1}0):(10\bar{1}1) =$ | | 68 54½ | 68 57⅓ |
| $m \cdot t = (01\bar{1}0):(02\bar{2}1) =$ | | 25 43 | 25 51 |
| $s \cdot R = (02\bar{2}1):(10\bar{1}1) =$ | | 51 14 | 51 12 |
| $r:R = (10\bar{1}1):(01\bar{1}1) =$ | | 42 8 | 42 5⅓ |
| $R:m = (10\bar{1}1):(10\bar{1}0) =$ | | 44 5 | 44 5¾ |
| $x:m = (22\bar{4}1):(10\bar{1}0) =$ | | 40 55₂ | 40 54¼ |
| $x:R = (22\bar{4}1):(01\bar{1}1) =$ | | 77 58 | 78 17 |
| $m:x = (01\bar{1}0):(22\bar{4}1) =$ | | 40 55½ | 40 54⅓ |
| $x:R = (22\bar{4}1):(10\bar{1}1) =$ | | 28 2 | 28 3 |
| $x:r = (22\bar{4}1):(01\bar{1}1) =$ | | 28 2 | 28 3 |
| $c:x = (0001):(22\bar{4}1) =$ | | 60 48 | 60 46½ |
| $x:x = (22\bar{4}1):(22\bar{4}1) =$ | | 58 24 | 58 23 |

Intergrowths of two crystals occur, with their trigonal axes intersecting under right angles, and one individual rotated about it through 180°.

The crystals are distinctly dichroitic: on $\{10\bar{1}0\}$ for vibrations parallel to the direction of the $c$-axis, they are orange, for vibrations perpendicular to the first, blood-red.

Plates parallel to $\{0001\}$ show in convergent polarised light the interference-image of an uniaxial crystal without circular polarisation: the bars of the black cross are regularly extended to the centre of the image. The character of the birefringence is negative for all colours, and it is strong. For $Na$-light is $n_o = 1{,}6052$. $n_e = 1{,}5804$; the birefringence is therefore 0,025.

When the axial image is very much enlarged. it appears, on closer examination, to be properly *biaxial*, with an extremely small apparent angle of the axes, and with the axial-plane perpendicular to one of the edges $c:r$. Although the rotatory power of the crystals is obviously very weak, it is, however, rather probable that they represent pseudo-symmetrical intergrowths of lamellae of lower symmetry.

§ 6. III. LAEVOGYRATE POTASSIUM-RHODIUM-OXALATE $(+ 1H_2O)$.

From the last mother-liquids, in which the more soluble strychnine-salt is accumulated, the laevogyrate salt, together with some

racemic oxalate, is obtained by means of *potassium-iodide*. First the less soluble racemic salt crystallizes in the form of fig. 2, subsequently the laevogyrate antipode in splendid, garnet-red, flattened crystals.

Commonly the external aspect is that of fig. 4*a*, with a flattening parallel two opposite faces of the rhombohedron, of which one is often excavated and uneven. Occasionally also crystals of the aspect
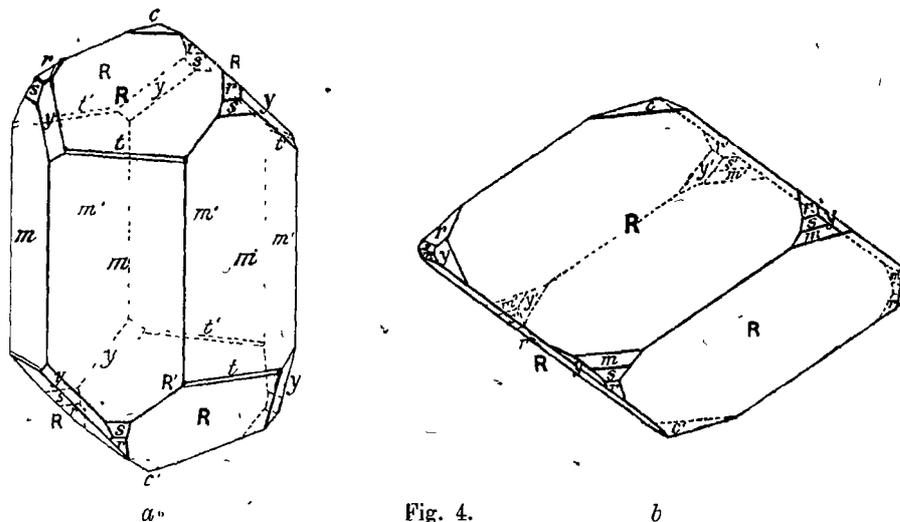


Fig. 4.

Laevogyrate Potassium-Rhodium-Oxalate (+ 1 $H_2O$).

of fig. 4*b* were obtained. Both combinations are also met with in the case of the dextrogyrate salt, but the antipodes differ in the occurring of a *left*-handed trigonal bipyramid $y = \{4\overline{22}1\}$ [75$\overline{1}$] in the *laevo*gyrate forms, where the dextrogyrate manifested the *right*-handed trigonal bipyramid $x = \{22\overline{4}1\}$ [715]. For the rest the angular values are the same as found in the case of the dextrogyrate salt. A review of some values may convince the reader of this:

| Angles: | Observed: | Calculated: |
|---|---|---|
| $R : R = (\overline{1}101):(10\overline{1}\overline{1}) =^*$ | 77° 0′ | — |
| $c : R = (0001):(10\overline{1}\overline{1}) =$ | 46 1 | 45°54′ |
| $c : r = (0001):(0\overline{1}\overline{1}1) =$ | 45 52 | 45 54 |
| $r : s = (01\overline{1}\overline{1}):(02\overline{2}\overline{1}) =$ | 18 3 | 18 15 |
| $s : m = (02\overline{2}\overline{1}):(01\overline{1}0) =$ | 26 0 | 25 51 |
| $m : t = (01\overline{1}0):(02\overline{2}\overline{1}) =$ | 26 1 | 25 51 |
| $y : m = (4\overline{22}1):(10\overline{1}0) =$ | 40 58 | 40 54 |
| $y : r = (4\overline{22}1):(\overline{1}\overline{1}01) =$ | 28 0 | 28 2 |
| $y : R = (4\overline{22}1):(\overline{1}\overline{1}0\overline{1}) =$ | 78 8 | 78 17 |

The geometrical as well as the optical properties, with the exception of the peculiarity just mentioned, are in both cases perfectly agreeing. There can be no doubt whatever as to the fact that the two optically active salts crystallise in non-superposable mirror-images, although the crystals themselves do not show a distinct rotatory power. Stereographical projections of the dextro- and laevogyrate crystal-forms are given here in fig. 5a and 5b, for the purpose of surveying the general zonal relations.
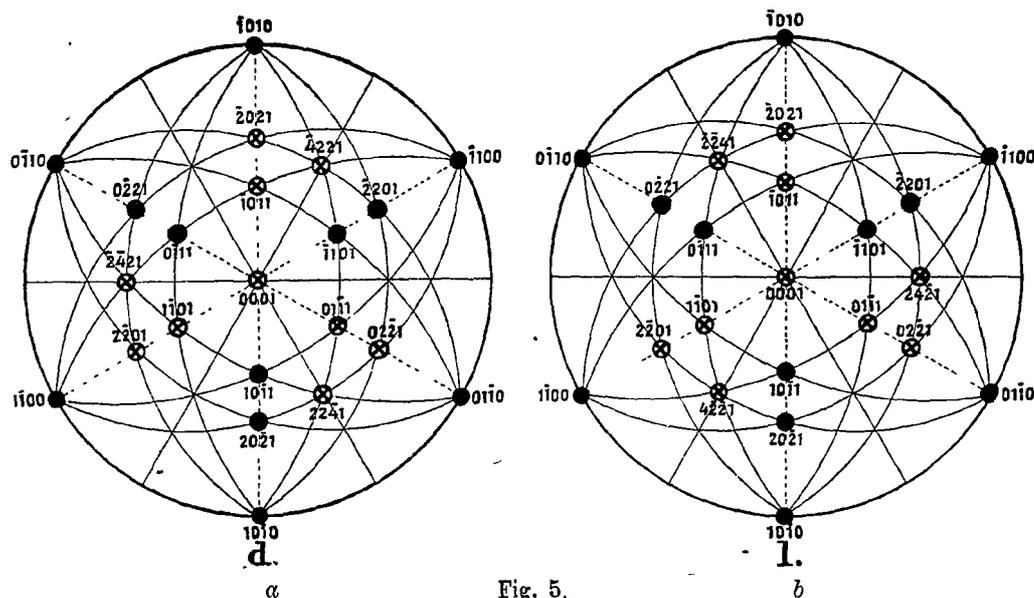


Fig. 5.

Stereographical Projection of the Crystal-forms of dextro- and laevo- Potassium-Rhodium-Oxalate. ($+ 1 H_2O$).

From these facts it becomes clearly evident that in the case investigated PASTEUR's principle appears fully confirmed. Indeed, a non-superposable hemihedrism of the crystal-forms can be stated as inseparably accompanying the enormously strong optical activity of the solutions of these salts. However, it is worth attention that even here this hemihedrism only manifests itself by the occurrence of a single trigonal bipyramid, and never by the presence of any "trapezohedral" face, as e.g. in the case of quartz; this fact again may in some way or other be connected also with the lack of chemical contrast between the dissymmetrically arranged substitutes.

Finally it may be remarked that a solution of these salts after three days, exposure to the light and even to the sun-light, did not exhibit any appreciable photochemical decomposition. In aqueous solution, however, the substance exposed in quartz-vessels to the

action of a strong *quartz*-lamp during some few hours, appeared decomposed to a detectable degree: metallic *rhodium* covered the walls of the *quartz*-apparatus in the form of a black mirror, while carbon-dioxide was set free. As the violet and blue rays are almost completely absorbed by the solutions (see above), the relatively rapid photochemical destruction of the molecule by rays of short wave-length may be considered as to be in full accordance with DRAPER's law.

§ **7**. If a solution of *potassium-rhodium-oxalate* be treated with *silver-nitrate*, the *silver*-salt: $\{Rho\,(C_2O_4)_3\}\,Ag_3$ is precipitated as a vividly red compound, which is only little soluble in cold, somewhat more in hot water, and which crystallises in long needles much alike the *bichromate*.

From this *silver*-salt, as well as directly from the *potassium*-salts, by interchange with *tri-ethylenediamine-rhodium-halogenides*, complex salts of the type $\{Rho\,(Eine)_3\}\,\{Rho\,(C_2O_4)\}_3$, may be obtained as pale yellow to orange-yellow crystalline precipitates, which are almost insoluble in all kinds of solvents. as was to be expected beforehand.

By combination of the *racemic* and optically-*active* ions, we have finally obtained the following nine isomeric salts:

$\{r\text{-}Rho\,(Eine)_3\}$ $\{r\text{-}Rho\,(C_2O_4)_3\}$; $\{r\text{-}Rho\,(Eine)_3\}$ $\{d\text{-}Rho\,(C_2O_4)_3\}$;
$\{r\text{-}Rho\,(Eine)_3\}$ $\{l\text{-}Rho\,(C_2O_4)_3\}$; $\{d\text{-}Rho\,(Eine)_3\}$ $\{r\text{-}Rho\,(C_2O_4)_3\}$;
$\{l\text{-}Rho\,(Eine)_3\}$ $\{r\text{-}Rho\,(C_2O_4)\}_3$; $\{d\text{-}Rho\,(Eine)_3\}$ $\{d\text{-}Rho\,(C_2O_4)_3\}$;
$\{l\text{-}Rho\,(Eine)_3\}$ $\{l\text{-}Rho\,(C_2O_4)\}_3$; $\{d\text{-}Rho\,(Eine)_3\}$ $\{l\text{-}Rho\,(C_2O_4)_3\}$;
and $\{l\text{-}Rho\,(Eine)_3\}$ $\{d\text{-}Rho\,(C_2O_4)_3\}$.

§ **8**. Furthermore some measurements may be recorded here concerning *potassium-rhodium-malonate*: $K_3\{Rho(C_3H_2O_4)_3\} + 3H_2O$, a new compound obtained in a way analogous to that described for the corresponding *oxalate*, and which is now also used in fission-experiments. Finally the description has been given here also of *potassium-iridium-oxalate*: $K_3\{Ir\,(C_2O_4)_3\} + 4\frac{1}{2}\,H_2O$, of which the fission into its antipodes is now being investigated also in the author's laboratory. The available data prove once more plainly the full *isomorphism* between *Rho*- and *Ir*-derivates of analogous structure.

§ **9**. RÁCEMIC POTASSIUM-RHODIUM-MALONATE.

$\{Rho\,(C_3H_2O_4)_3\}\,K_3 + 3H_2O.$
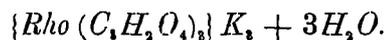
This compound was prepared from freshly precipitated and washed *rhodium-hydroxyde*, by boiling it during a long time with a solution of *potassium-bimalonate*, to which some *free malonic acid* was added. Complete solution occurs only after heating during a very

long time; moreover the salt is more easily hydrolysed than the corresponding *oxalate*. It contains 9,32 % of water, corresponding to the presence of three molecules of crystallisation-water.

The salt crystallises from an aqueous solution in the form of thin, hexagonally bordered, orange-red plates, or occasionally in somewhat thicker crystals, exhibiting however the same combination-forms. They show appreciable oscillations of their angular values.

*Monoclinic-prismatic.*

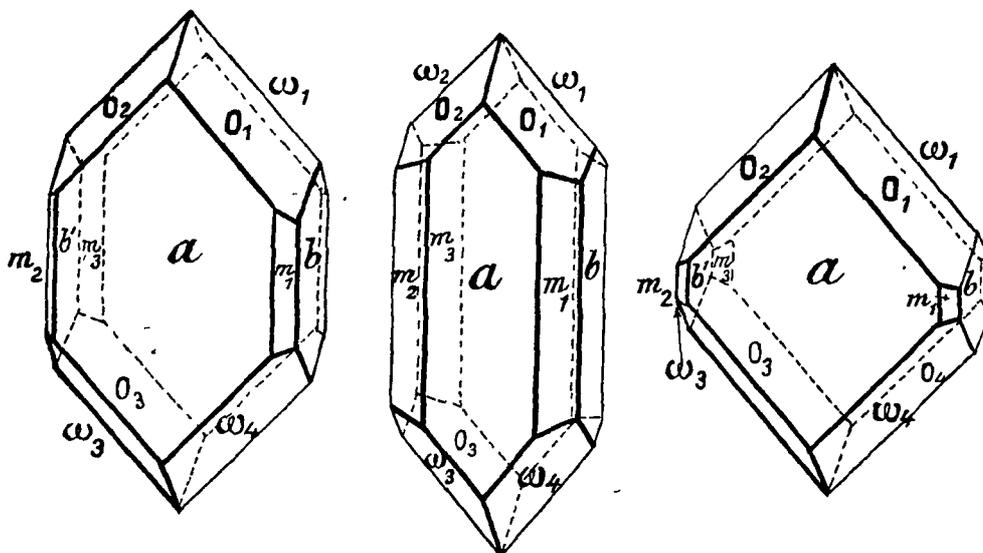$$a : b : c = 1,2309 : 1 : 1,0783 ; \quad \beta = 86°36'.$$



Fig. 6.

Racemic Potassium-Rhodium Malonate (+ 3 $H_2O$).

*Forms observed*: $a = \{100\}$, always predominant and very lustrous; $o = \{111\}$ and $\omega = \{\bar{1}11\}$, commonly equally large, occasionally $o$ much broader than $\omega$, and yielding sharp reflexes; $m = \{210\}$, larger or smaller, but always well reflecting; $b = \{010\}$, ordinarily narrow, often absent, sometimes even broader than $m$. The external habit is that of plates parallel to $\{100\}$, with a slight elongation in the direction of the c-axis.

| Angles: | Observed: | Calculated: |
|---|---|---|
| $b : o = (010) : (111) =^*$ | 51°48' | — |
| $a : o = (100) : (111) =^*$ | 57 30 | — |
| $w : a' = (\bar{1}11) : (\bar{1}00) =^*$ | 60 55 | — |
| $a : m = (100) : (210) =$ | 31 32 | 31°34' |
| $m : b = (210) : (010) =$ | 58 28 | 58 26 |
| $o : o = (111) : (1\bar{1}1) =$ | 76 15 | 76 24 |
| $o : \omega = (111) : (\bar{1}11) =$ | 61 40 | 61 35 |
| $\omega : \omega = (\bar{1}11) : (\bar{1}\bar{1}1) =$ | 79 20 | 79 44 |
| $b : \omega = (010) : (\bar{1}11) =$ | 50 25 | 50 8 |

No distinct cleavability has been found. At {100} corrosion-figures having the shape of isosceles triangles were observed; their symmetry is in accordance with that of the monoclinic-prismatic class. The crystals are only feebly dichroitic. The plane of the optical axes is {010}; one optical axis is observable at the border of the optical field, under appreciable inclination to the plane {100}. The dispersion is inclined and weak, with $\varrho > v$. The birefringence has negative character.

## § 10. Racemic Potassium-Iridium-Oxalate ($+ 4\frac{1}{2}H_2O$).

The substance was obtained by dissolving freshly precipitated *iridium-hydroxide* in *oxalic acid*. The process goes on extremely slowly and is accomplished only by heating during about 30 hours at a reflux-cooler, until the liquid has got a pure yellow colour. It is then neutralized with *potassium-carbonate* and slowly evaporated at room-temperature[1]). Besides much *potassium-oxalate*, orange coloured crystals of the *iridium*-salt are deposited. They are selected, purified, and recrystallised several times from aqueous solutions.

The salt is deposited from aqueous solutions in beautiful orange crystals, which are very lustrous and suited for precise measurements.
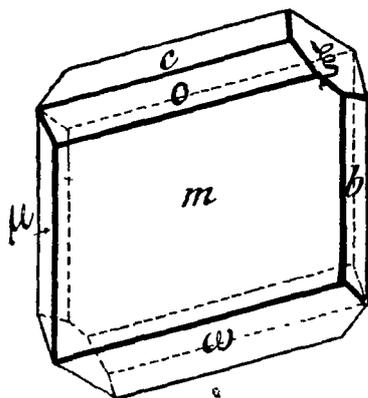
Fig. 7.

Racemic Potassium-Iridium-Oxalate

($+ 4\frac{1}{2} H_2O$).

*Triclinic-pinacoidal.*

$a : b : c = 1,0771 : 1 : 1,0405;$

$A = 93° 22\frac{1}{2}'.$    $\alpha = 98° 38\frac{1}{2}'.$
$B = 101° 36\frac{3}{4}'.$    $\beta = 104° 3'.$
$C = 67° 27'.$    $\gamma = 66° 9\frac{1}{2}'.$

*Forms observed*: $m = \{110\}$, predominant, much larger than $\mu = \{1\bar{1}0\}$, and $b = \{010\}$; the vertical zône exhibits occasionally appreciable fluctuations of the angular values, and multiple reflexes; $c = \{001\}$, smaller than $\mu$, but very lustrous; $o = \{111\}$, a little larger than $c$, and $\omega = \{1\bar{1}1\}$,

much broader than $o$; all three forms yield very good reflexes; $\xi = \{\bar{1}12\}$, large and very lustrous. The external form appears flattened parallel to $m$; the plates are commonly very thick.

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[1]) Cf. G. Gialdini, Rend. Acad. Linc. Roma (5ª). **16.** II. 551. (1907); the crystals were measured by F. Zambonini, (Zeits. f. Kryst. u. Min. **47.** 621, (1910), who also demonstrated their isomorphism with the analogous rhodium-compound However, his interpretation of the occurring forms is different from the one given by us.

| Angles : | Observed: | | Calculated |
|---|---|---|---|
| | (JAEGER): | (ZAMBONINI): | |
| $m:b$ $= (110):(010) =^*$ | 53°54' | 53° 59' | -- |
| $m:\omega$ $= (110):(1\bar{1}\bar{1}) =^*$ | 45 33 | 45 30 | — |
| $b:\mu$ $= (0\bar{1}0):(\bar{1}\bar{1}0) =^*$ | 32 40 | 32 37 | — |
| $c:\mu$ $= (00\bar{1}):(\bar{1}\bar{1}0) =^*$ | 94 40 | 94 38 | — |
| $c:m$ $= (001):(110) =^*$ | 76 40 | — | — |
| $\dot{m}:\nu$ $= (110):(1\bar{1}0) =$ | 93 20 | 93 24 | 93°26' |
| $\nu:\omega$ $= (1\bar{1}0):(11\bar{1}) =$ | 96 25 | 96 18 | 96 30⅓ |
| $c:\xi$ $= (00\bar{1}):(1\bar{1}2) =$ | 43 42 | — | 43 59 |
| $m:o$ $= (110):(111) =$ | 34 38 | — | 34 20 |
| $c:o$ $= (001):(111) =$ | 42 20 | — | 42 20 |
| $c:\omega$ $= (00\bar{1}):(11\bar{1}) =$ | 57 46 | 56(?)46 | 57 46 |
| $m:\xi$ $= (110):(\bar{1}12) =$ | 78 13 | — | 77 59 |
| $\omega:\xi$ $= (11\bar{1}):(1\bar{1}2) =$ | 70 17 | 70 16 | 70 13 |
| $\nu:\xi$ $= (1\bar{1}0):(\bar{1}12) =$ | 50 58 | 50 51 | 51 45 |
| $a:\nu$ $= (100):(1\bar{1}0) =$ | — | — | 34 47 |
| $a:m$ $= (100):(110) =$ | — | — | 58 39 |

No distinct cleavability was found.

On all faces oblique extinction. The crystals are strongly dichroitic: on $m$ yellow and orange, quite analogous to the corresponding *rhodium*-compound. --

There can be no doubt about the complete *isomorphism* of the crystals in this case with those of the *Rho*-salt. The corresponding *Co*-salt was investigated by COPAUX; it is also triclinic-pinacoidal, but not isomorphous with the two other salts, probably because of a difference in its content of water of crystallisation. Attempts will be made to obtain the analogous *cobalti*-salt.

Afterwards we will communicate in detail about our fission-experiments of *potassium-rhodium-malonate* and of *potassium-iridium-oxalate*, as soon as their optical antipodes will have been obtained.

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