

Citation:

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Chemistry. — “Investigations on PASTEUR’S Principle concerning the Relation between Molecular and Crystallonomical Dissymmetry: V. Optically active complex-salts of Iridium-Trioxalic Acid”. By Prof. F. M. JAEGER.

(Communicated in the meeting of June 29, 1918).

§ 1. A short time ago I published¹⁾ some data about the properties of *racemic Potassium-Iridium-Oxalate*: $\{K, Ir (C, O)_3\} + 4\frac{1}{2} H_2O^2)$, and on that occasion I announced experiments undertaken with the aim of splitting this compound into its optical antipodes. It was our purpose to gain in this way the necessary information to enable us to indicate the correct configuration in space of these optically active complex ions, in comparing it with that attributed to the corresponding *rhodium*-derivatives, in consequence of the arguments brought forward on that occasion. At the same time I hoped to investigate in this way, what influence the substitution of the central *rhodium*-atom in these complex ions by the homologous *iridium*-atom appeared to have upon the magnitude and the specific character of the optical rotation and its remarkable dispersion. It may be considered of importance, of course, to know the relation existing between the two functions just mentioned, especially in connection with our former studies on the analogously constituted complex salts of *cobalt* and *rhodium* combined with three molecules of *ethylenediamine*, where the problem arose as to the true configurative relations between the salts of these homologous metals of the eighth group of the periodic system, when rotating the plane of polarisation in the same direction³⁾.

In the following the fission-experiments mentioned and the results obtained by them are recorded in details. Thus for the first time the possibility of a “partial” asymmetry⁴⁾ has been proved, in the case of *iridium* as the central atom; the series of the metals showing

¹⁾ F. M. JAEGER, *Proceed. R. Acad. Amsterdam*. **20**. 263. (1917).

²⁾ C. GIALDINI, *Rend. Acad. d. Linc., Roma*, (5a), **16**. II. 551. (1907); *Proceed. Acad. Amsterdam*, loco cit. p. 278.

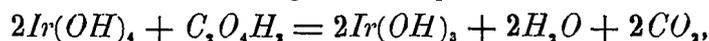
³⁾ F. M. JAEGER, *Proceed. R. Acad. Amsterdam*, **17** 49. (1915); **20**. 244. (1917); *conf. Zeits. f. Kryst. u. Mner.* **55**. 209. (1915).

⁴⁾ F. M. JAEGER, *Lectures on the Principle of Symmetry, Amsterdam*, (1917), p. 235.

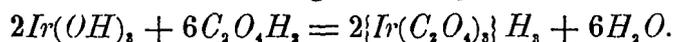
this phenomenon being herewith extended to *chromium, iron, cobalt, platinum, rhodium, and iridium*. With respect to the dispersion of some of these salts, we hope yet to furnish some new data in the near future.

§ 2. The required *racemic Potassium-Iridium-Oxalate*: $K_3\{Ir(C_2O_4)\} + 4\frac{1}{2}H_2O$ was obtained in the following way. A 3% solution of pure, hydrated *iridiumchloride* of commerce (HERAEUS) is treated by a solution of *potassiumhydroxide* in excess. A dirty brownish precipitate is formed, which dissolves in the excess of *KOH* to form *potassium-iridiate*. The alkaline solution is heated, and then some *perhydrol* (30% H_2O_2) added: the colour changes to dark blue, and the principal part of the *iridium* precipitates as $Ir(OH)_4$. Another part of it remains in the solution as a colloidal suspension of great stability, not being precipitated or coagulated from it, even after addition of electrolytes. These solutions are therefore better evaporated, and the residue transformed into *ammonium-chloro-iridiate* to be used afterwards in other experiments.

The blue precipitate is washed by decantation with water slightly acidified by means of *oxalic acid*; the filtrates and washings are also later converted into the mentioned compound. When the removed liquid gets colourless, the decantation may be considered complete, and the precipitate is brought into a round bottom flask, the superfluous liquid removed after some hours, standing, and a hot, concentrated solution of *oxalic acid* added. The contents of the vessel are boiled under a reflux-condenser during 30 or 40 hours, a part of the *oxalic acid* is thereby decomposed, and the tetravalent *iridium* reduced to trivalent according to the equation:



while *iridium-trioxalic acid* is then formed from the derivative of the trivalent *iridium*, conforming to the equation:



The gold-yellow solution finally obtained is filtered, and almost perfectly neutralised by means of $KHCO_3$; it is then concentrated on the waterbath, and the successive fractions of the crystals formed are separately collected. Almost pure *potassium-oxalate* is first deposited, and afterwards, besides this, the orange crystals of the salt required, which is very soluble. These crystals have to be separated mechanically, and they are afterwards recrystallised for purification¹⁾.

The *racemic* compound crystallises in pale orange-coloured crystals,

¹⁾ Dr. J. KAHN has aided most effectively in the preparation of a part of this *racemic* compound, and in the troublesome working up of the *iridium*-residues.

which have already been investigated and described in a former paper¹⁾. They are triclinic-pinacoidal, and completely isomorphous with the corresponding racemic *rhodium*-salt, so that the direct isomorphous substitution of the metals *Rho* and *Ir*, also in their complex salts, has been hereby definitely proved. As we shall see, this proof has now also been given in the case of the *optically-active components* of such complex salts.

§ 3. *Fission of the racemic Potassium-Iridium-Oxalate* ($+4\frac{1}{2}H_2O$) *into its optically-active components.*

27,5 Grams of pure *strychnine-nitrate* are dissolved in 1300 ccm. boiling water; then a solution of 15,5 grams of the racemic salt in 250 ccs water of 60° C. is rapidly poured into the boiling solution under perpetual stirring. The flask with the golden yellow liquid is allowed to cool slowly for twelve hours to room-temperature. The deposited, highly yellowish coloured, felty-like crystals are sharply sucked off at the water-pump, washed with some strong alcohol, afterwards with some ligroine, and dried at room-temperature in an air-current. The mother-liquid is evaporated on the waterbath to about $\frac{2}{3}$ of its original volume; on cooling highly yellow, needle-shaped crystals are again deposited, which are treated in the same way. While the first fraction, however, represents the *strychnine*-salt of the *dextrogyratory* component, — the *laevogyrate* antipode was immediately obtained from the second precipitate. On further evaporation of the filtrate, some paler coloured fractions are consecutively obtained, all of which give the *laevogyratory potassium*-salt. The sixth and the seventh fraction finally consisted of pure *strychnine*, accompanied by some of its *nitrate*, while in the last fractions crystals of the free, *racemic potassium*-salt together with some of the *laevo*-salt, and also some *potassium-nitrate*, appeared. The rotation of this last fraction as a whole, after removing the *potassium-nitrate*, was negative, amounting only to about $\frac{1}{7}$ of the rotation of the pure *laevogyrate* salt, so that a considerable amount of racemic salt is evidently admixed. Probably a partial hydrolysis during the repeated evaporations has taken place, so that the free *potassium*salt accumulates in the last fractions.

The *strychnine*-salt of the *dextrogyratory* component has the formula: $\{Ir(C_2O_4)_3\}_2(C_{21}H_{22}N_2O_2)_2 + 3\frac{1}{2}H_2O$; it appears as pale yellow, very fine needles. For a series of wave-lengths the rotation of this strongly active salt was determined; the solution used contained 0,4763 grams of the hydrated salt in 100 ccs. of the liquid.

¹⁾ F. M. JAEGER, Proceed, R. Acad. Amsterdam, 20, 278, (1917).

The following data were found:

ROTATION-DISPERSION OF STRYCHNINE- <i>d</i> -IRIDIUM-OXALATE (+ 3½ H ₂ O).		
<i>Wave-length in A. U.:</i>	<i>Observed Rotation:</i>	<i>Molecular Rotation:</i>
5105	+ 1.02	+ 20997°
5260	0.86	17703
5430	0.65	13379
5610	0.38	7822
5800	0.27	5558
6020	0.21	4323
6260	0.17	3499
6530	0.15 ^s	2676

In the same way the composition of the corresponding *strychnine*-salt of the *laevogyrate* component appeared to be: $\{Ir(C_2O_4)_3\}C_{21}H_{22}N_2O_2 + 3H_2O$. This salt too crystallises in needles, somewhat thicker than those of the first. The substance is strongly *laevogyra*-tory, and its dispersion is smaller than in the case of the other salt, as may be seen from the following data, and the graphic representation in fig. 1:

ROTATION-DISPERSION OF STRYCHNINE- <i>l</i> -IRIDIUM-OXALATE (+ 3 H ₂ O).		
<i>Wave-length in A. U.:</i>	<i>Observed Rotation:</i>	<i>Molecular Rotation:</i>
5105	- 0.33	- 17236°
5260	0.28	14624
5430	0.24	12535
5610	0.19	9994
5800	0.15	7835
6020	0.12 ^s	6057
6260	0.09	4701
6530	0.08	4178

This solution contained 0,1886 grams of substance in 100 grams of the liquid.

It is remarkable that the laevogyrate *strychnine*-salt has a somewhat greater molecular rotation than the corresponding *potassium*-salt itself; the dextrogyrate *strychnine*-salt rotates more strongly than the free *potassium*-salt.

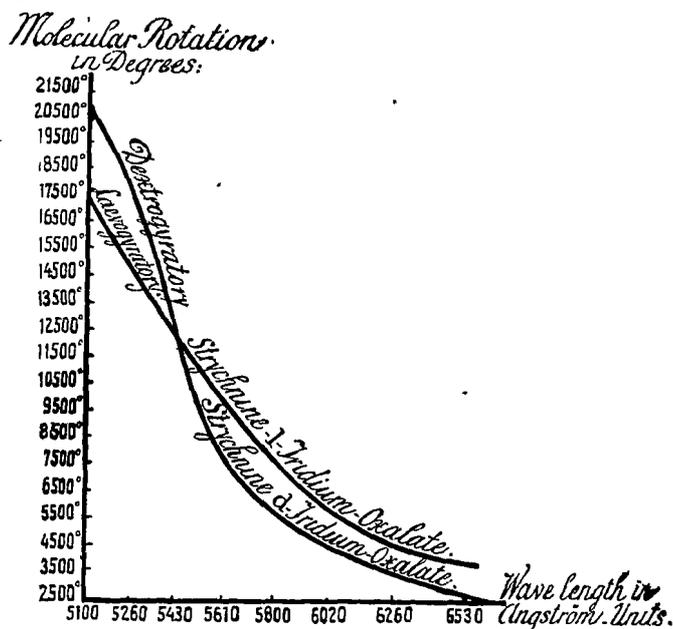


Fig 1. Molecular Rotation Dispersion of Strychnine- α -Iridium-Oxalate ($\frac{1}{2}$ H₂O) and of Strychnine- β -Iridium-Oxalate ($\frac{1}{2}$ H₂O).

§ 4. The different fractions were mixed with about six times their weight of finely pulverized *potassium-iodide*, and then ground together in a mortar, some cold water being added to the mixture. When all *potassium-iodide* has just been dissolved, the yellow liquid is sharply sucked off from the white precipitate, this last washed with a very small quantity of cold water, and the yellow filtrate precipitated by the addition of an excess of 95 % alcohol. A yellow deposit is formed, which is sucked off on the BUCHNER-filter, washed with alcohol, and recrystallised from water. On heating on the waterbath the solution does not autoracemise notably. By slow crystallisation at roomtemperature, beautiful trigonally-shaped, orange crystals are formed, which are dried between filterpaper. They can grow in their mother-liquid to considerable size. The optically-active components are extremely soluble, more than the very soluble racemic compound; on this account the crystallisation of the active components was executed in smaller and somewhat deeper crystallisation-dishes.

§ 5. The rotation-dispersion of these optically-active *iridium*-salts was measured in the same way as formerly by means of a great polarimeter of SCHMIDT and HAENSCH, with threefold field, and equipped with a monochromator. The tube was always 20 cm. long, and determinations were made for a whole series of wave-lengths. Even in thin layers of the liquid the spectral region of the transmitted light appeared to be appreciably limited by absorption, also in the case of not very concentrated solutions.

Waves larger than 6850 A.U. were never transmitted to a sufficient degree, while even in a solution of 1% no exact determinations could be made for wave-lengths smaller than 5300 A.U. To investigate the shape of the dispersion-curve also for shorter wavelengths, it was therefore necessary to use very dilute solutions, of 0,2% and 0,1% or less. We have used four such solutions for this purpose, containing respectively one grammolecule of the hydrated salt in 14,57 Liters (*a*) of the solution, in 57,73 Liters (*b*), in 228,86 Liters (*c*), and in 413,7 Liters (*d*).

In the following table the mean values are taken into account, and the molecular rotations calculated from them; in fig. 2 these results are moreover graphically plotted, in their relation to the light used:

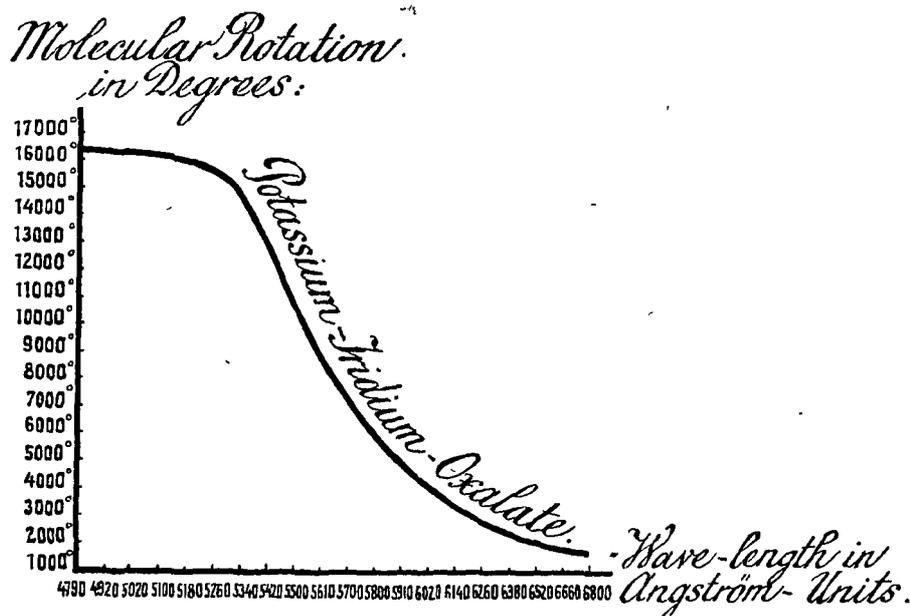


Fig. 2. *Molecular Rotation-Dispersion of the Optically active Potassium-Iridium-Oxalates.*

The values obtained with the different solutions agreed very well

together. In the table are therefore quoted those values which approached nearest to the curve of the mean values. The dispersion-curve shows a tendency to get more and more horizontal for wave-lengths beneath 5100 A.U.

ROTATION-DISPERSION OF DEXTROGYRATE POTASSIUM-IRIDIUM-OXALATE (+ 1 H ₂ O).		
<i>Wave-length in A. U.:</i>	<i>Observed Rotation in Degrees:</i>	<i>Molecular Rotation in Degrees:</i>
4790	+ 0.79 (a)	+ 16340°
4920	0.785 (a)	16237
5020	0.78 (a)	16134
5100	0.78 (a)	16134
5180	0.77 (a)	15927
5260	0.75 (a)	15514
5340	1.28 (c)	14647
5420	4.36 (b)	12586
5510	14.42 (a)	10508
5610	11.94 <i>id.</i>	8699
5700	9.88 <i>id.</i>	7198
5800	8.17 <i>id.</i>	5952
5910	6.86 <i>id.</i>	4998
6020	5.49 <i>id.</i>	4000
6140	4.73 <i>id.</i>	3446
6260	3.86 <i>id.</i>	2813
6380	3.32 <i>id.</i>	2446
6520	2.61 <i>id.</i>	1901
6660	2.33 <i>id.</i>	1698
6800	2.10 <i>id.</i>	1530

Although the dispersion of these orange-coloured solutions is extraordinarily strong, the slope of the curve is quite different from that found in the case of the corresponding *rhodium*-salt. This fact proves the preponderant influence of the special nature of the

central metal-atom on the specific light-absorption (colour) of these salts and on the whole character of the rotation-dispersion.

The yellow crystals obtained on evaporating the original mother-liquid of the *strychnine*-salts to $\frac{2}{3}$ or $\frac{1}{2}$ of its volume, gave after treatment with potassium-iodide a fraction which appeared to be the *pure laevogyrate* salt. The following measurements, made with a solution containing one grammolecule of the hydrated salt in 42.97 Liters of the liquid, may make this clear:

ROTATION-DISPERSION OF THE LAEVOGYRATE POTASSIUM-IRIDIUM-OXALATE (+ 1H ₂ O).		
<i>Wave-length in A. U.:</i>	<i>Observed Rotation in Degrees</i>	<i>Molecular Rotation in Degrees:</i>
5340	- 6° 66	- 14287°
5430	5.72	12289
5520	4.89	10506
5610	3.86	8293
5700	3.26	7004
5800	2.70	5801
5910	2.28	4898
6020	1.95	4189
6140	1.63	3502
6260	1.35	2900
6340	1.07	2299
6520	0.88	1891
6660	0.74	1590
6800	0.70	1504

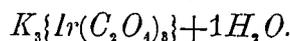
A comparison of the rotations for the same wave-lengths in the case of the corresponding *rhodium*-salt with the here described

<i>Salt:</i>	<i>Molecular Rotation:</i>	<i>Atomic Volume of the metal:</i>
$K_3 \{Rho(C_2O_4)_3\} + H_2O.$	$M_{4930} = 14200^\circ; M_{5800} = 790^\circ; M_{5970} = 0^\circ; M_{6660} = -1215^\circ$	8.50
$K_3 \{Ir(C_2O_4)_3\} + H_2O.$	$M_{4930} = 16230^\circ; M_{5800} = 5952^\circ; M_{5970} = 4500^\circ; M_{6660} = +1698^\circ.$	8.61

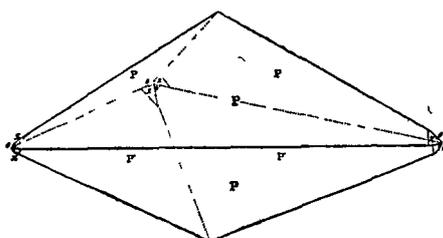
iridium-salts, teaches us, that the rotation of the *iridium*-salt is always appreciably *greater* than that of the *rhodium*-salt, although the atomic volume of *iridium* differs only slightly from that of *rhodium*, and even exceeds it by a small amount.

If we were able to demonstrate later, that for $\{Ir(Aeïne)_3\}I_3$, the rotations are smaller than those of the corresponding *rhodium*-salt, then we should have proved that the influence of the atomic volume on the magnitude of the rotation, may be in this or in the opposite direction, according to there being either basic or acid substituents attached to the central-atom.

§ 6. DEXTROGYRATORY POTASSIUM-IRIDIUM-OXALATE:



Beautiful, rather large, orange-coloured, and very lustrous crystals, which are commonly regularly developed in the shape of flattened, triangular bipyramids. They are well built and geometrically easily determinable, allowing very exact measurements. The deviations of the angular values from those found with the corresponding *rhodium*-



Dextrogyratory Potassium-Iridium-Oxalate.

Fig. 3.

salt are more appreciable than ordinarily stated in the case of rigorously isomorphous crystals.

The symmetry of the two series of crystals is however exactly the same, and their form-analogy is sufficiently great, to consider the optically-active salts of the two series as quite isomorphous, also with respect to the doubtless isomorphy between the racemic salts of the *rhodium*-, and the *iridium*-series. The more deviating values of the angles and axial parameters are probably connected with the rather great difference of atomic weight of the metal-atoms. Analysis teaches us, that also these optically-active salts crystallise with only one molecule of water.

Trigonal-trapezohedral.

$$a : c = 1 : 0,9520. \text{ (BRAVAIS); } \alpha = 100^{\circ}20'. \text{ (MILLER).}$$

Forms observed. $P = \{11\bar{2}2\} [52\bar{1}]$, as positive trigonal bipyramid,

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predominant and yielding good reflexes; $o = \{10\bar{1}1\}$ $[100]$, positive rhombohedron of the first kind, well reflecting, but in most cases only with rather small facets; $x = \{1\bar{1}01\}$ $[\bar{2}\bar{1}2]$, a negative rhombohedron of the first kind, commonly much broader than o , somewhat less lustrous; $y = \{2\bar{1}\bar{1}1\}$ $[4\bar{2}1]$, a negative trigonal bipyramid, about as large as x , but much smaller than P , commonly yielding good mirror-images; $r = \{1\bar{1}02\}$, as a narrow obtusion of the edges of the rhombohedron o , ordinarily absent, but in the other case very lustrous. Sometimes a very narrow and rudimentarily developed prism $m = \{11\bar{2}0\}$ was observed, truncating the basal edges of P . The crystals are mostly very regularly developed as flat trigonal bipyramids; but occasionally more or less deformed, table-shaped individuals are met with, showing the same combination of forms. The faces of P are often striated parallel to the edges $P: o$. (Fig. 3). Also crystals are found, where o is about twice as large as P ; in this case the striation on P was observed in all cases.

Finally we met with individuals showing only P and o in about equal size, P having its characteristic striation; besides them also y was found occasionally, but very small and subordinate, especially in the case of the dextrogyrate component.

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$P: P'' = (11\bar{2}2): (1\bar{2}12) = *$	73° 20'	—
$P: P' = (11\bar{2}2): (11\bar{2}\bar{2}) =$	92 49	92° 49'
$P: o = (11\bar{2}2): (10\bar{1}1) =$	21 40	21 43
$x: o = (1\bar{1}01): (10\bar{1}1) =$	43 28	43 26
$x: y = (1\bar{1}01): (2\bar{1}\bar{1}1) =$	28 20	28 21
$y: o = (2\bar{1}\bar{1}1): (10\bar{1}1) =$	28 24	28 21
$P: o = (1\bar{2}12): (10\bar{1}1) =$	60 48	60 50½
$o: o = (10\bar{1}1): (0\bar{1}11) =$	79 30	79 40
$o: r = (10\bar{1}1): (1\bar{1}02) =$	39 43	39 50
$m: P = (11\bar{2}0): (11\bar{2}2) =$	46 30	46 25

No distinct cleavage was observed.

Optically uniaxial, without noticeable circular polarisation. The character of the birefringence is negative.

The specific gravity of the crystals at 20° C. was: 2,734; the molecular volume is therefore: 217,77, and the topical parameters are: $\chi: \omega = 7,0618: 6.7230$, if calculated with respect to hexagonal axes, and $\chi = \psi = \omega = 6,1321$, with respect to rhombohedral axes.

§ 7. The crystals of the laevogyrate antipode ordinarily showed only the bipyramid P , which must be considered as a *lefthanded* bipyramid here, because all phenomena are in agreement in this case with PASTEUR'S law, as is proved beyond doubt by the hemihedral symmetry of the crystals. Therefore to this bipyramid must be attributed the symbol $\{2\bar{1}\bar{1}2\} [5\bar{1}2]$, besides the forms o , x , and y , y having the symbol $\{11\bar{2}1\} [4\bar{1}2]$, appear subordinately here. Because o and x were in most crystals about equally large, and could not be discerned in any other way, the external habit of these lefthanded crystals was not different from that of dextrogyrate salt, the latter being brought into the same position as the lefthanded by a rotation through 60° round the trigonal axis, with the only difference, that the forms x and o are thereby interchanged. However, if x and o are of unequal size, the occurrence of mirror-images could be seen immediately in the crystals. The zonal relations may be made clear by the subsequent stereographical projections (Fig. 4). Just as in the case of oppositely rotating *rhodium*-salts, a non-superposable hemihedrism accompanies here the contrary power of rotation.

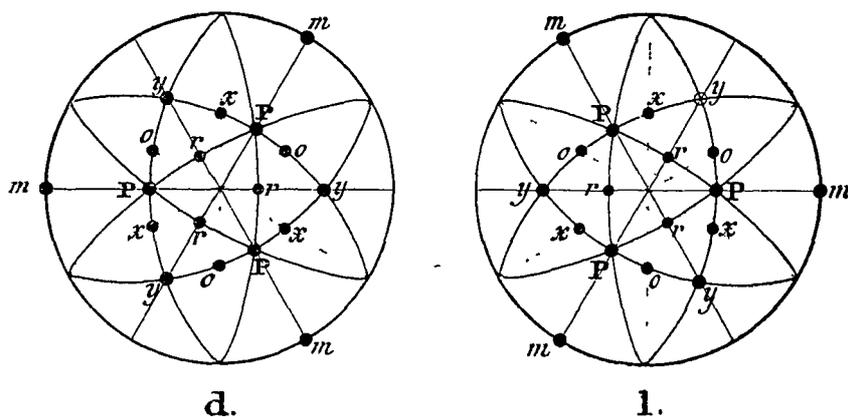


Fig. 4. Stereographical Projection of the Crystalforms of *d*- and *l*-Potassium-Iridium-Ovalate (only the top-ends of the crystals).

§ 8. The specific gravities of the formerly investigated *rhodium*-salts, were determined at $d_{40}^{20} = 2,171$ for the racemic compound ($4\frac{1}{2} H_2O$), corresponding to a molecular volume of 260,34; and at $d_{40}^{20} = 2,255$ for each of the optically-active salts ($+ 1H_2O$), which corresponds to a molecular volume of 222,70. From this the topical axes of these salts are calculated at:

$\chi : \psi : \omega = 6,8980 : 6,4274 : 6,6306$, for the racemic *rhodium*-salt, and $\chi : \omega = 7,2660 : 6,4944$, for the optically-active salts, with respect to hexagonal axes, and $\chi = \psi = \omega = 6,1856$, with respect to rhombohedral axes.

Comparison with the corresponding parameters of the here studied *iridium*-salts ¹⁾:

Salt:	Topical Parameters:
racemic $K_3 \{ Rho (C_2 O_4)_3 \}, 4\frac{1}{2} H_2O$.	$\chi : \psi : \omega = 6,8980 : 6,4274 : 6,6306$.
racemic $K_3 \{ Ir (C_2 O_4)_3 \}, 4\frac{1}{2} H_2O$.	$\chi : \psi : \omega = 6,7454 : 6,2626 : 6,5162$.
optically-active $K_3 \{ Rho (C_2 O_4)_3 \}, H_2O$.	$\chi : \omega = 7,2660 : 6,4944; \chi' = 6,1856$.
optically-active $K_3 \{ Ir (C_2 O_4)_3 \}, H_2O$.	$\chi : \omega = 7,0618 : 6,7230; \chi' = 6,1321$.

teaches us, that the substitution of the central *Rho*-atom in the complex oxalate by the isomorphous *Ir*-atom, produces a diminution of the topical parameter ω in the case of the racemic salts, but a slight increase, in the case of the optically active antipodes, although the values for χ and χ' are in this case smaller with the corresponding *Rho*-salt.

In the same way as in the case of the previously described *rhodium-oxalate*, all phenomena observed in the fission of *potassium-iridium-oxalate* are really in full agreement with the sense of PASTEUR'S law.

*Laboratory for Inorganic and Physical
Chemistry of the University.*

Groningen, June 1918.

¹⁾ The specific gravity of racemic $K_3 \{ Ir (C_2 O_4)_3 \} + 4\frac{1}{2} H_2O$ was at 18° C. determined at: $d_{20}^{20} = 2,688$; the molecular volume is thus: 243,82.