Chemistry. — *On Pterotactic Derivatives of Bivalent Platinum with Optically-active, Cyclic trans-1-2-Diamines.* By F. M. JAEGER and J. TER BERG.

§ 1. In this paper a series of complex salts of *bivalent platinum* with racemic and optically active *cyclopentane-trans-1-2-diamines* and *cyclohexane-trans-1-2-diamines* are described, which probably present some structural peculiarities hitherto not met with in such compounds.

For the preparation of these salts of bivalent *platinum*, 12 grammes of K_2PtCl_4 are dissolved on the water-bath in as little hot water as possible and then 6 grammes of the base are added to the solution. After some moments the red colour of the latter disappears and a heavy, orange-yellowish precipitate is formed; this is the very sparely soluble compound containing only 1 molecule of the base. When adding to the solution still 3 grammes of the base, the precipitate is, after heating the solution in a closed flask on the water-bath during many hours, finally dissolved to a yellowish coloured liquor. This is filtered and left standing for some time; then the cooled solution is mixed with about 800 cc of alcohol. The salt is slowly precipitated as a white crystalline powder; after 24 hours it is filtered off and recrystallized from as little boiling water as possible. The alcoholic mother-liquor, after being neutralized with *HCl*, is evaporated on the water-bath and, besides *KCl* and the hydrochloride of the base present in excess, still yields a certain quantity of the impure compound, which can be purified by repeated crystallizations from boiling water. In the reactions with the *optically active* bases only *one* salt is generated, with a yield about equal to the calculated quantity. The pure salts thus obtained are perfectly colourless; the derivatives of the optically active bases, in general, prove better to crystallize than those obtained from the racemic bases. The latter *platinum*-compounds originally appear to be deposited as opaque, small spherolithes, which under the microscope appear as aggregates of ten or twelve round-edged individuals without definite forms and only weakly birefracting. Often the rounded lumps have a more flattened, more or less irregularly tabular aspect.

§ 2. On the other hand the salts containing two molecules of the optically-active bases immediately crystallize from their aqueous solutions in the shape of small, lustrous, colourless, apparently quadratic plates. A more detailed study revealed that they are not tetragonal, but truly *rhombic-*

F. M. JAEGER AND J. TER BERG: ON PTEROTACTIC DERIVATIVES OF BIVALENT PLATINUM WITH OPTICALLY-ACTIVE, CYCLIC TRANS-1-2-DIAMINES.
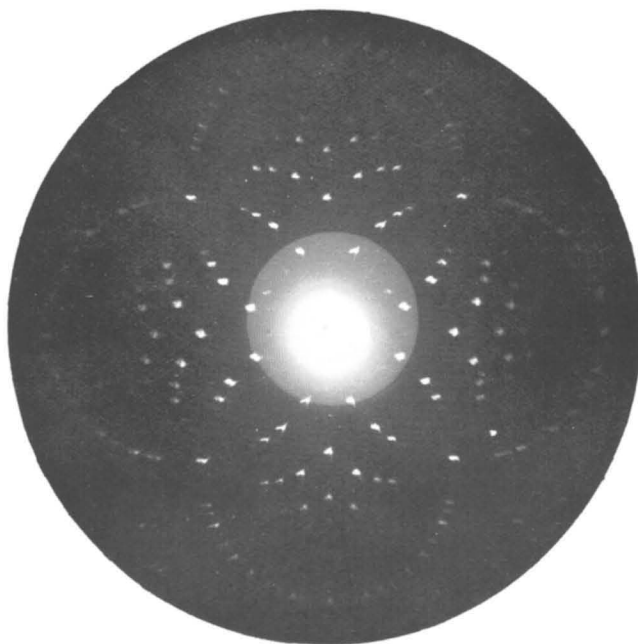

Fig. 1a. *X-ray Pattern of D-{Pt (l-Cptn)$_2$}Cl$_2$ perpendicular to {001};*
(tungsten-K-α-radiation) 35 K.V.
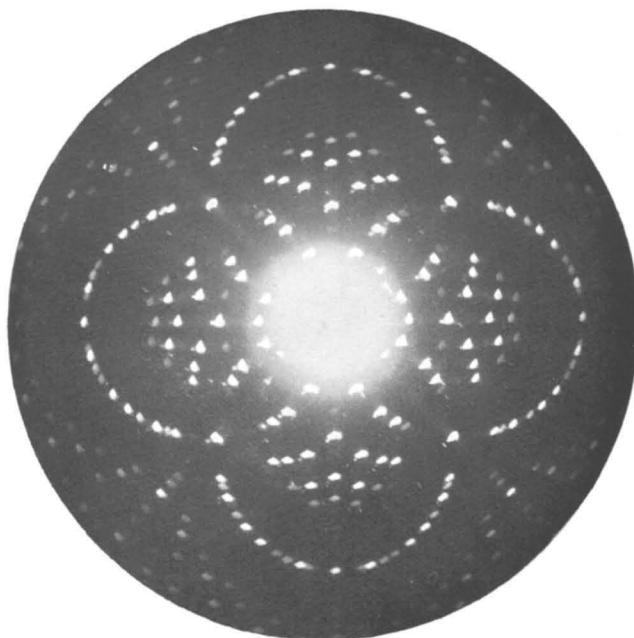
Fig. 1b. *X-ray Pattern of D-{Pt (l-Chxn)$_2$}Cl$_2$ perpendicular to {001};*
(tungsten-K-α-radiation) 35 K.V.

bisphenoidal and *pseudo-tetragonal* to such a degree that their axial ratio: $a : b$ cannot be distinguished from *unity* and that their deviation from true tetragonal symmetry is, in their LAUE-ray patterns perpendicular to {001}, either not at all, or only manifested by the mere presence or absence of a few diffraction-spots in the zones closely situated round the central spot. The two diffraction-patterns of this kind reproduced in Figs. 1*a* and 1*b* of the Plate clearly demonstrate the only small deviations from a perfectly tetragonal symmetry and also the close analogy in the architecture of these crystals, which evidently must be considered as truly *isomorphous*, — as also had already been deduced from the crystallographical measurements. The patterns were obtained with *tungsten*-radiation (35 Kilovolts); they here appear on the same scale (distance of film to crystal = 5 c.M.). Evidently the first pattern does *not* manifest any observable deviation at all from true tetragonal symmetry.
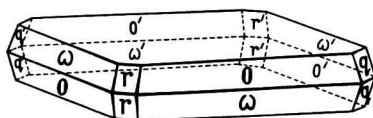
The salts crystallize in the form of Fig. 2.

Fig. 2. *Crystalform of* D-{Pt(l-Cptn)₂}Cl₂ *and of* D-{Pt(l-Chxn)₂}Cl₂.

D-$\{Pt(l\text{-}Cptn)_2\}Cl_2$ has the axial ratio : $a : b : c = 1 : 1 : 2,937$.

The forms observed are: $c = \{001\}$, large and lustrous;

$o = \{111\}$ and $\omega = \{1\bar{1}1\}$, narrow, about equally developed;

$r = \{101\}$ and $q = \{011\}$, both small, equally developed an well measurable.

Angular Values:

$$c : r = (001) : (101) = 71° \ 12'.$$
$$c : r = (001) : (111) = 76° \ 28'.$$

The crystals are optically biaxial, but D-$\{Pt(l\text{-}Cptn)_2\}Cl_2$ is almost uniaxial : the plane of the optical axes is {100}, with the c-axis as the first bisectrix of positive character. The apparent angle of the axes is very small.

A perfect cleavability occurs parallel to {001}. By means of oscillation-spectrograms, the parameters of the elementary cell were determined to be : $a_0 = b_0 = 8,10$ Å.U.; $c_0 = 23,5$ Å.U. The cell contains 4 times the molecular mass; the specific gravity of the crystals is: 2,061.

D-$\{Pt(l\text{-}Chxn)_2\}Cl_2$ has the axial ratio: $a : b : c = 1 : 1 : 3,163$, with the same limiting faces as the former salt. The angular values are : $(001) : (111) = 77° \ 24'$ and $(111) : (1\bar{1}1) = 87° \ 16\frac{1}{2}'$. The plane of the optical axes is {100}; the angle of the axes is small, but greater than in the first case. The c-axis is the first bisectrix; the double-refraction is positive, the

dispersion of rhombic character: $\varrho < \nu$. The crystals are perfectly cleavable parallel to {001}.

From X-ray spectrograms round the principal axes, the parameters of the elementary cell, which contains 4 molecules of the salt, were calculated to be: $a_0 = b_0 = 8,10$ Å.U.; $c_0 = 25,2$ Å.U. The density is: 1,952.

§ 3. In solution the two salts are strongly *dextro*gyratory for all wavelengths between 4200 and 7000 Å.U.; i.e. their rotation is *opposite* to that of the bases present in their complex ions.

The molecular rotations $[M] \cdot 10^{-2}$ of these salts, together with those of the free bases of *opposite* rotation [1]), are graphically represented in Fig. 3.
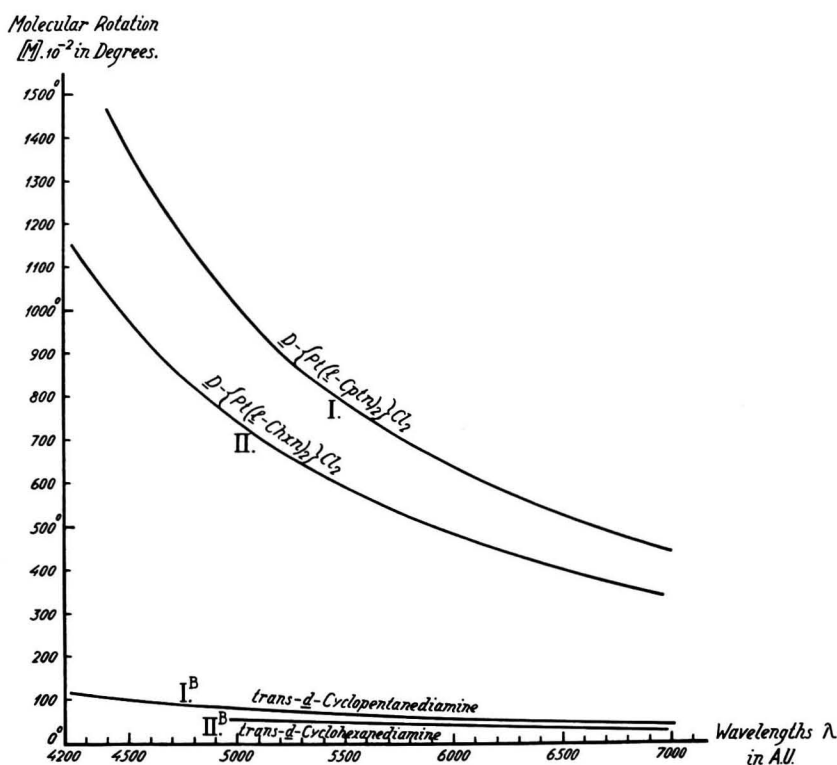

Fig. 3. *The Molecular Rotations* $[M] \cdot 10^{-2}$ *of* D-{Pt (l-Cptn)$_2$} Cl$_2$ *and*
D-{Pt (l-Chxn)$_2$} Cl$_2$ a d of d-Cyclopentane- and d-Cyclohexane-diamines.

§ 4. From these data it at once becomes clear that the rotation of these salts is not only opposite to that of the bases contained in them, but that this opposite rotation is also *appreciably* greater than that of the free diamines themselves; their rotatory influence in the complex ion appears at different wavelengths to be enlarged in a ratio of at least about 13 to 15

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[1]) F. M. JAEGER and L. BIJKERK, these Proceed., **40**, 12, 22, (1937); F. M. JAEGER and H. B. BLUMENDAL, Zeits. f. anorg. Chemie, **175**, 168, 169, (1928).

	Rotatory Dispersion of Di-*l*-Cyclopentanediamine- and of Di-*l*-Cyclohexanediamine-Plato-Chlorides in Aqueous Solution.			
Wavelength λ in A.U.:	Specific Rotation [α] of D-{Pt(l-Cptn)₂} Cl₂:	Molecular Rotation [M] . 10⁻² of D-{Pt(l-Cptn)₂} Cl₂:	Specific Rotation [α] of D-{Pt (l Chxn)₂} Cl₂:	Molecular Rotation [M] . 10⁻² of D-{Pt (l-Chxn)₂} Cl₂:
6980	+88.3	+443	+68.3	+337
6730	97.7	490	75.3	372
6480	107.0	532	82.4	407
6262	115.0	577	89.3	441
6074	124.0	622	95.8	473
5893	133.6	667	102.1	504
5735	142.1	712	109.1	539
5592	150.3	757	115.9	573
5463	159.8	802	122.8	607
5340	169.4	850	129.2	638
5224	179.6	899	135.9	671
5126	189.0	948	142.6	705
5036	199.2	996	149.2	737
4950	208.7	1045	155.7	769
4862	218.3	1094	161.6	798
4793	227.8	1142	167.7	828
4724	236.4	1188	173.7	858
4658	245.9	1232	181.3	896
4596	254.9	1280	186.9	923
4537	264.4	1328	193.3	955
4483	276.1	1377	200.1	988
4430	283 4	1426	205.9	1017
4380	—	—	212.3	1048
4335	—	—	216.7	1070
4290	—	—	223.3	1103
4248	—	—	232.4	1148

The salts: L-{Pt) d-Cptn)₂} Cl₂ and L-{Pt (d-Chxn)₂} Cl₂ show the same rotations, but with opposite algebraic signs.

times by the linkage of these bases into the atomic cycles including the central *platinum* atom.

Now the two bases are *trans*-substitution-products, as is proved by their resolvability into optical antipodes: this means that the two NH_2-groups are situated at *opposite* sides of the mean plane of the carbon-rings. In the case of the *cyclohexanediamine* with its *puckered* carbon-cycle, there are at least two ways in which the molecule can be attached to the central atom; but *cyclopentanediamine,* having a *flat* carbon-cycle, can only be linked to it in a single way. Even if the four valencies of the bivalent *platinum*-atom, according to WERNER's original hypothesis, are supposed to be situated *in the same plane,* — the two molecules of the *cyclopentanediamine* must be inserted into the complex ion in an *oblique* position, twisted with respect to each other like the wings of a stirrer or propeller; and the ion as such will thus have a single binary axis of symmetry perpendicular to the plane of the four valencies of the *platinum*-atom and two binary axes in that plane, bisecting the right angles between those four *Pt*-valencies. This is exactly the symmetry of the rhombic-bisphenoidal class.

The special way of linkage here described of the two cyclic systems to the central metallic atom, may be indicated as a *pterotactic* [1]) one and has to be distinguished from the "spirane" like structures, as observed in carbon-compounds. Such a pterotactic arrangement lowers the degree of symmetry of the complex ion in such a way that all planes of symmetry necessarily must disappear and the whole architecture only can preserve an *axial* symmetry. This axial symmetry is in full agreement with the strong optical activity exhibited by the ion and with the *exclusive* generation of only a single, optically active compound in the evidently "dissymetrical" reaction between K_2PtCl_4 and the dextro- or levogyratory bases used. Taking into account the fact of the complete analogy, of the crystal forms of the *dicyclopentanediamine-* and *dicyclohexanediamine-plato-*derivatives as well as of their *X*-ray patterns, — it is evident that the two kinds of complex salts also possess *the same* structural character of their cations; i.e. it can be considered as certain that the way of insertion of the two cyclic bases into each of those complex ions has occurred in exactly the same way. Thus the *dicyclohexanediamine-plato-chloride* also must be considered to be a typical "pterotactic" compound and its rotatory properties are, therefore, quite analogous to those of the *dicyclopentanediamine* salt previously dealt with.

§ 5. The salts of this pterotactic type: $D\text{-}\{Pt(l\text{-}Base)_2\}Cl_2$ and $L\text{-}\{Pt(d\text{-}Base)_2\}Cl_2$, if combined in equimolar quantities, will yield a *racemic* compound of the constitution:
$[D\text{-}\{Pt(l\text{-}Base)_2\}Cl_2 + L\text{-}\{Pt(d\text{-}Base)_2\}Cl_2]$; this true racemate will, of course, by appropriate means, be resolvable into its optical antipodes.

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[1]) From: *pteron* = wing and *tattein* = arrange.

By means of X-ray experiments it could, moreover, be proved beyond any doubt that this "racemate" and the optically *inactive* product, which was obtained by the direct interaction between K_2PtCl_4 and the *racemic* base, are indeed rigorously *identical*. These racemates obtained from the inactive *cyclohexane-* and the *cyclopentanediamines,* — juist like the optically active salts of the two bases with respect to each other, — also proved to be quite isomorphous.

Their *d-tartrates* could be obtained as crystalline products which, however, hitherto could not be separated into fractions of different solubility and specific rotation, so as to lead to a direct fission into their antipodes.

The *d-tartrate* obtained is very soluble; but on slow evaporation of the solution it readily crystallizes. Small, opaque crystals, which soon loose their water of crystallization.

Monoclinic-sphenoïdal.
$$a : b : c = 0{,}688 : 1 : 1{,}528;$$
$$\beta = 46° 12'.$$

Forms observed: $m = \{110\}$ and $\{p = \{1\bar{1}0\}$, also $c = \{001\}$, about equally large; $q = \{011\}$ and $r' = \{\bar{1}01\}$ well developed; $\omega' = \{\bar{1}11\}$, smaller than q; $t = \{0\bar{1}1\}$, often absent or small; $s' = \{\bar{1}03\}$, small; $x' = \{\bar{1}1\bar{3}\}$, somewhat larger than s'; $o = \{1\bar{1}1\}$, mostly absent, small. (Fig. 4).

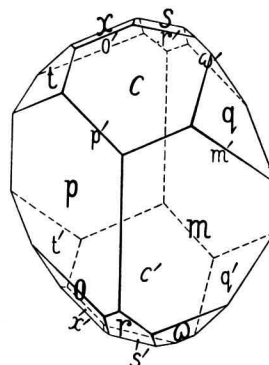Fig. 4. *Crystalform of*
$\{Pt(r.Chxn)_2\}d\text{-}C_4H_4O_6 + \frac{1}{2}H_2O$

Angular Values:		Observed:		Calculated:	
$c : s'$	$= (001) : (\bar{1}03) =$	*47°	38'	—	
$s' : r'$	$= (\bar{1}03) : (\bar{1}01) =$	*60	54	—	
$m : p$	$= (110) : (1\bar{1}0) =$	*52	50	—	
$m : c$	$= (110) : (001) =$	51	32	51°	18'
$m : s'$	$= (110) : (\bar{1}03) =$	93	50	93	26
$s' : x'$	$= (\bar{1}03) : (\bar{1}1\bar{3}) =$	26	55	26	57
$c : q$	$= (001) : (011) =$	47	24	47	48
$c : \omega'$	$= (001) : (\bar{1}11) =$	105	22	105	26
$r' : o'$	$= (\bar{1}01) : (1\bar{1}1) =$	33	0	33	7

The angular values oscillate considerably, often about 0°,5. No distinct cleavability was observed.

§ 6. However, still another optically *inactive* compound has, — from the theoretical point of view, — to be expected, in which one molecule of the *dextro-* and one molecule of the *levogyratory* base simultaneously may be

present: then the planes of the two pterotactically linked molecules necessarily would be *equally* inclined and directed with respect to the plane of the four *Pt*-valencies and, therefore, this time within the complex ions will be inclined in *the same* sense. This ion thus should possess a plane of symmetry Σ perpendicular to the plane of the four *Pt*-valencies and, therefore, it could by no means ever be resolved into optically active components. The new inactive salt in this respect thus would completely behave like *meso-* (or *anti-*)-*tartaric acid* in comparison to the resolvable *racemic acid*. One could expect that perhaps it might be generated, if the *racemic* bases were made to react with K_2PtCl_4, — at least when it is supposed that there is no particular reason of stability, which presumably would exclude the possibility of simultaneous introduction of a dextro- and a levogyratory molecule into one and the same complex ion, — as such a hindrance certainly was stated by us [1]) to exist in the case of the *tri-diamino-cobaltic* salts of the optically active diamines under consideration. In the latter case such kind of "mixed" ions, — if generated at all, — proved in solution always to be decomposed into a mixture of the corresponding salts containing three molecules of only the bases with *the same* direction of rotation. In this case the resolvable *in*active compounds could be demonstrated also to be built up from the *D-* and *L*-antipodes when combined in equal number of molecules. As, however, at least in principle, there is *no* such opposite tendency to a simultaneous introduction of two molecules of oppositely rotating bases into the same complex ion present, — we must conclude that, in the case of the pterotactical linkage of such diamines, the possible existence of *four* isomerides must be taken into account: namely the *D-* and *L*-salts already described, the resolvable *racemate* of the latter und the *un*resolvable *meso*-form just mentioned.

Because the inactive reaction-product of the racemic base with K_2PtCl_4 proved to be identical with the true racemate generated by mixing equimolar quantities of the *D-* and *L*-compounds, evidently there was no chance of catching this expected *meso*-form in the two ways described.

§ 7. The only way still possible for trying the preparation of $\left\{Pt\left(\begin{array}{c}d\text{-}Chxn\\l\text{-}Chxn\end{array}\right)\right\}Cl_2$ was heating K_2PtCl_4 with half the calculated quantity of *d-cyclohexanediamine* and separating this product from the reaction-mixture, then subsequently heating this purified product with exactly the calculated quantity of *l-cyclohexanediamine* in aqueous solution and precipitating the product now generated by means of an excess of absolute alcohol. Thus a wite, crystalline salt was obtained, which was recrystalized from as little water of 80° C. as possible, by slow evaporation of the saturated solution at room-temperature. First crystallized the typical

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[1]) F. M. JAEGER and L. BIJKERK, these Proceed., **40**, 256, 325, (1937).

spherolithes and flat, rounded aggregations already described, which evidently represented the anhydrous racemic salt previously mentioned : its identity with the racemate, as well as with the $\{Pt(rac.Chxn)_2\}Cl_2$ obtained from the racemic base, was, moreover, demonstrated by means of its X-ray spectrogram. After some days *another* colourless salt started to crystallize from the mother-liquor in small, parallelogram-shaped tables and in well-developed thicker crystals. They were separated from the solution and found to be optically *inactive* in solution. On analysis they proved to yield :

Pt : 32,76—32,80 %; N : 9,52—9,62 %; H_2O : 17,82 %; Cl : 11,73 %.

Evidently, the composition of this salt is: $\{Pt(rac.Chxn_2\}Cl_2 + 6H_2O$; calculated: 32,42 % Pt; 9,30 % N; 17,94 % H_2O and 11,79 %. In solution it does not manifest any optical rotation.

The compound, on measurement with the theodolite-goniometer, proved to be *triclinic-pinacoidal*.

The compound crystallizes in small colourless and lustrous crystals which usually are tabular parallel to $\{001\}$.

Triclinic-pinacoidal.

$$a : b : c = 0,891 : 1 : 0,987.$$

$A = 84°48'$; $a = 98°26'$
$B = 77\ 15$; $\beta = 104\ 21$
$C = 102\ 42$; $\gamma = 75\ 41$

Fig. 5.

Rac. $\{Pt(Chxn)_2\}Cl_2 + 6\,H_2O.$

Forms observed :

$a = \{100\}$; $b = \{010\}$; $c = \{001\}$,

the latter form often predominant, so that the crystals are parallelogram-shaped; $r = \{101\}$; $s = \{\bar{1}01\}$; $q = \{011\}$; $t = \{0\bar{1}1\}$; $m = \{110\}$; $M = \{1\bar{1}0\}$; all about equally broad.
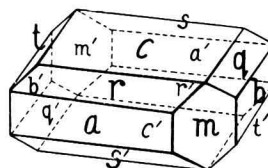
Angular Values:	*Observed*:	*Calculated*:
$b : m = (010) : (110) =$ *56° 10′	—
$m : a = (110) : (100) =$ *46 32	—
$a : c = (100) : (001) =$ *77 15	—
$c : b = (001) : (010) =$ *84 48	—
$b' : t = (0\bar{1}0) : (0\bar{1}1) =$ *47 59	—
$a : M = (100) : (1\bar{1}0) =$ 35 34	35° 34′
$a : r = (100) : (101) =$ 35 43	35 50
$c : m = (001) : (110) =$ 75 18	75 12
$c : M = (001) : (1\bar{1}0) =$ 84 31	84 26
$c : s = (001) : (\bar{1}01) =$ 55 52	55 47
$b' : q = (010) : (011) =$ 42 40	42 43
$b : s = (010) : (\bar{1}01) =$ 75 24	75 15

33*

No distinct cleavability was observed.

On {001} the extinction is oblique: about 40°—42° with respect to the direction of the b-axis; one dark hyperbola is eccentrically visible.

After carefully dehydrating the salt, an X-ray spectrogram was made of the remaining white anhydrous powder: this proved to be *completely identical* with the spectrograms obtained with the two optically inactive salts previously prepared. From this the conclusion must be drawn that, beyond any doubt, the triclinic salt described solely represents an *hexahydrate of the racemic compound* and consequently *is not* the *meso*-salt here looked for.

Evidently, therefore, also in this case the simultaneous introduction of two molecules of the oppositely rotating bases into the complex ion seems to be impossible under the circumstances mentioned: in solution two molecules of the salt obtained immediately prove to be changed into an equimolecular mixture of the corresponding salts with two dextro- and two levogyratory molecules of the base respectively.

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Chemistry. — *The constitution of toxoflavin.* (Provisional communication.) By A. G. van VEEN and J. K. BAARS.

(Communicated at the meeting of May 29, 1937.)

Some years ago we described the isolation and properties of toxoflavin[1], one of the two very violent poisons that can be formed by the action of Bacterium cocovenenans. This bacterium, which was discovered by MERTENS and van VEEN, is the cause of the well-known bongkrek- and semaji-poisonings met with in Java.

Toxoflavin crystallises in yellow needles, melts at 171° and gives an intensely yellow-coloured solution in water. The aqueous solution has a neutral reaction and is stable only between pH$_3$ and pH$_8$. By the action of sulphite and other reducing agents, toxoflavin is reduced to a colourless compound; after shaking with air the yellow colour returns. The substance is very stable to bromine, nitric acid, nitrous acid, and other oxidants and possesses no NH$_2$- or other reactive groups.

The pharmacological investigation on rabbits was made by DARWIS AMAR and A. GREVENSTUK[2] who showed that toxoflavin is a violent

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[1] A. G. van VEEN and W. K. MERTENS, Proceedings Royal Acad. Amsterdam **36**, 666, (1933); Rec. Trav. Chim. **53**, 257, 398 (1934).
[2] Geneesk. Tijdschr. v. N. I. **75**, 104 (1935).