Chemistry. — *On Complex Salts of Trivalent Rhodium with α-α'-Dipyridyl.*
By F. M. JAEGER and J. A. VAN DIJK.

(Communicated at the meeting of April 28, 1934.)

§ 1. If *α-α'-dipyridyl* is made to react with soluble *rhodiumchloride*: $RhCl_3 + 4H_2O$ or with *sodium-rhodiumchloride*: $Na_3\{RhCl_6\} + 12H_2O$ under different circumstances, several types of complex salts are obtained. The content of *dipyridyl* of those salts is dependent on the relative quantities of the base added and on the nature of the solvent applied. The formation of *mono-*, *di-* and *tri-dipyridyl*-complexes of trivalent rhodium could be stated with certainty; but in all cases the simultaneous formation of at least two of such types of salt was observed. This fact renders the investigation of these salts and their isolation in the pure condition extremely difficult, because the intermixed salts, once formed, can in most cases not be separated from each other, — most probably as a consequence of their gradual hydrolysis and of the formation of solid solutions between them. In general the solubility in water of the three types of salts mentioned proves to increase with the content of dipyridyl in the complex ion: while the salts of the *tri-dipyridylrhodium*-ion are highly soluble in water, alcohol, etc., those derived from the *mono-dipyridylrhodium*-ion often are either practically insoluble or only very sparely soluble in the same solvents. Nor is the solubility of the *di-dipyridylrhodium*-salts very considerable, but yet it is greater than that of the *mono-dipyridylrhodium*-derivatives. As in the observed, simultaneous production of these salts, hydrolysis-phenomena evidently play an important rôle, the reaction products are, in each reaction, more or less differently coloured — the colour being dependent on the quantity of the admixed by-product. For the same reason their analysis often yields deviating percentages of the constituents, — a fact which is connected with the different circumstances of concentration, solvent, etc. during their preparation. In the beginning the analysis of these compounds presented great difficulties; especially the exact estimation of the rhodium present was very difficult, because these complexes often are either very stable and then can be decomposed only with difficulty, or they are less stable and then become hydrolysed. The best way of analysis finally proved to consist in very carefully melting the salts with sodiumhydroxide in nickel crucibles and in determining the rhodium as metallic rhodium, after reduction in a current of hydrogen. The content of nitrogen was volumetrically determined, after combustion, by micro-analysis. The water present ordinarily could not completely be driven-out at 100° C., but was eliminated at that temperature only partially: the remaining part of it then must be estimated by taking the difference of the sum of the percentages of *Rh, Cl, dipyridyl*, etc. from 100 %.

§ 2. Because the facts observed are most unambiguous in the case of the *di-* and *tri-dipyridyl*salts, we will start with the description of the latter ones.

If 6,5 g. of finely-powdered $RhCl_3$, 4*aq.* are dissolved in 15 g. of boiling dipyridyl, the mixture then is heated for ten minutes and, after some alcohol and water being added, the preparation is subsequently heated on the waterbath for several hours; — an initially produced, brown-red precipitate appears to get gradually dissolved, with the exception of a small residue of reduced rhodium. The hot solution, after filtration, on cooling gradually proves to deposit a pale yellow product *A*. The filtered, brownish motherliquor is several times extracted with ether, for removing some free dipyridyl present, and subsequently concentrated on the waterbath. As the viscous liquid does not very readily crystallize, the greater part of the solved substance *B* contained in it can afterwards be precipitated by the addition of an excess of alcohol: the precipitate thus obtained is almost colourless, manifesting only a pale yellowish hue.

1. The yellow compound *A* can be recrystallized from an excess of boiling water, from which it is deposited in brilliant, pale yellow, rather small and thin crystalline tables. Their analysis gave: *Rh* 18,78 %; *Cl* 19,08 %; *N* 9,98 % (=55,7 % dipyridyl) and 6,4 % H_2O (95° C.); calculated for $\left\{ Rh \begin{matrix}(Dip)_2\\ Cl_2\end{matrix} \right\} Cl + 2H_2O$: *Rh* 18,5 %; *Cl* 19,1 %; *N* 10,1 % (=55,9 dipyridyl) and 6,3 % H_2O.

Often the colour of all the complex salts of this type is more orange-yellowish, — which is caused by a slight admixture of the corresponding, more brownish-yellow or orange-yellow *mono-dipyridylrhodium*-salt: indeed, such higher coloured products always yield somewhat too high percentages for *Rh* and *Cl* and, in general, the higher, the more intensive their colouring appears. This is in accordance with the fact, that the composition of the mono-dipyridylsalts of different composition show contents of rhodium lying between 23,5 to 26,5 % and of chlorine between 24,5 and 27,8 %.

The pure yellow product has two *Cl*-atoms within its complex nucleus: only *one third* of its chlorine proves to be ionogen. Thus, 0,1480 g. of the salt yielded 0,0408 g. *AgCl*, or 6,8 % ionogen chlorine. Its composition, therefore, is analogous to the corresponding *tetrapyridine*-salt described by JÖRGENSEN [1]). It is, however, only a byproduct in the reaction mentioned: its quantity formed is no more than about 5 % of that of the compound *B* simultaneously produced.

2. The compound *B* can be recrystallized from boiling alcohol. In contrast to the salt just described, the *total* quantity of its chlorine proves

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[1]) S. M. JÖRGENSEN, Journ. f. prakt. Chemie, (2), **27**, 478, (1883).

to be ionogen. The analysis gave: Rh 14,8 % ; Cl 14,76 % ; N 11,5—11,9 % ; calculated for $\{Rh(Dip)_3\}\ Cl_3 + 3H_2O$: Rh 14,5 % ; Cl 15,0 % ; N 11,8 %. The salt is often coloured more or less yellowish by a slight admixture of a blood-red substance, — perhaps: $\left\{ Rh_2 \begin{matrix}(Dip)_3\\ Cl_6\end{matrix} \right\}$, — which is very soluble in alcohol and cannot be completely separated from the complex salt itself; the blood-red impurity is deposited from the latter motherliquors in the shape of microscopically small, very thin, monoclinic plates [1]) with hexagonal boundaries.

The complex salt B mentioned crystallizes in the rhombic system (Fig. 1) and proves to be isomorphous with the corresponding cobaltic salt ($+ 2H_2O$). The crystalform of the colourless and of the more or less reddish or yellowish coloured crystals proves to be the same.

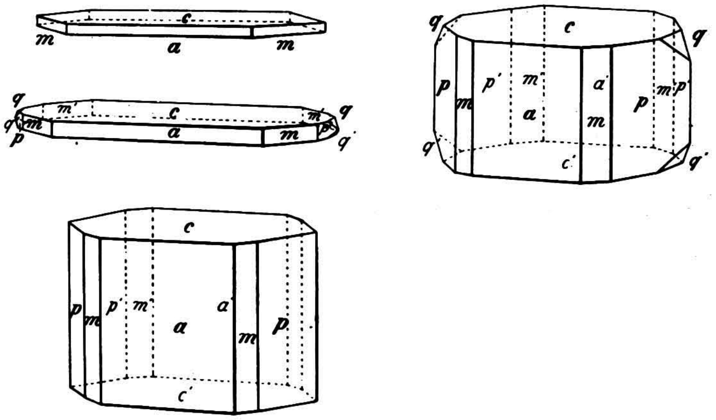

Fig. 1. Crystalforms of $\{Rh\,(Dip)_3\}\ Cl_3 + 3H_2O$.

Rhombic-bipyramidal.

$$a : b : c = 0{,}8591 : 1 : 1{,}4605$$

Forms observed: $a = \{100\}$, well reflecting, although yielding multiple images; $m = \{110\}$, very lustrous; $p = \{120\}$, less brilliant than m, ordinarily narrower, sometimes totally absent, but occasionally broader than m; $q = \{011\}$, very small and badly measurable, mostly absent. The crystals are prismatic parallel to the c-axis, or, mostly, needle-shaped parallel to the b-axis.

Angular Values:	*Observed*:	*Calculated*:
$a : m = (100) : (110) =^*$	40° 40′	—
$c : q = (001) : (011) =^*$	55 20	—
$m : p = (110) : (120) =$	19 14	19° 19′
$p : p = (120) : (\bar{1}20) =$	60 23	60 32

No distinct cleavability was observed.

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[1]) The plane of the optical axes is $\{010\}$; on $\{001\}$ one of the axes can be observed Inclined dispersion.

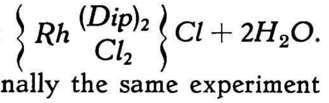
The plane of the optical axes is {010}; the first bissectrix is parallel to the c-axis and the apparent axial angle is only small.

Tentatives to remove the colouring matter by extraction with alcohol, acetone or chloroform in a SOXLETT-apparatus had no result: the subsequent fractions appear, without any regularity, more or less intensively coloured.

§ 3. If 9 g. of $Na_3\{RhCl_6\} + 12H_2O$ be dissolved in water (40 c.cm.) and, on heating on the waterbath, 6 g. of dipyridyl in alcoholic solution be added, the dark red solution suddenly becomes pale orange-red and subsequently the precipitation of the yellow product *A* sets in. In the remaining mother-liquor a small quantity of the *tri-dipyridyl*salt *B* is present besides the salt *A*: in this reaction the salt *A* formed now is the principal product, its quantity being about 37 times as great as that of *B*, — just the reverse of what was the case in the reaction between dipyridyl and $RhCl_3$, 4 *aq*. Also when $Na_3\{RhCl_6\} + 12H_2O$ is directly mixed with the base in aqueous solution and heated on the waterbath, almost exclusively the yellow *di-dipyridyl*salt *A* is formed; in the latter case the amount of the blood-red pigment formed proves to be greater than in the first case.

The preparation of the salt *A* was varied in several ways. 2,81 g. of $RhCl_3$, 4 *aq*., dissolved in acetone, were treated on the waterbath with 3,2 g. of dipyridyl; as no reaction occurred in this way, a certain quantity of methylalcohol was added. After 24 hours the liquid was evaporated almost to dryness and the orange-coloured mass extracted with absolute alcohol. The brown to brownish-yellow product, on analysis, yielded 21,43 % *Rh*; 24,17 % *Cl*; 8,26 % *N*; 8,4 % H_2O. From the mother-liquor a perfectly yellow product was obtained with: 19,47 % *Rh*; 19,87 % *Cl*; 9,29 % *N*; 9,51 % H_2O. Both products evidently consist of the *di-dipyridyl*-salt, mixed with variable quantities of the *mono-dipyridyl*-salt.

In another experiment 2,81 g. of $RhCl_3 + 4H_2O$ were finely pulverized and thoroughly mixed with 3,2 g. of finely-powdered dipyridyl; the mixture was heated till the base was boiling and then the mass heated on the waterbath with absolute alcohol. The filtered solution, after 24 hours' standing, proved to have deposited a yellow precipitate, besides some black, metallic rhodium; this yellow product, on analysis, yielded: 18,69 % *Rh*; 19,01 % *Cl*; 10.01 % *N*; 6,5 % H_2O, and evidently consisted of almost pure



$$\left\{ Rh \begin{matrix}(Dip)_2\\ Cl_2\end{matrix} \right\} Cl + 2H_2O.$$

Finally the same experiment was repeated with the equivalent quantity of finely-powdered $Na_3\{RhCl_6\} + 12H_2O$ and the orange-coloured mass thus produced extracted with hot water. The pale orange-coloured product now gave, on analysis: 22,5 % *Rh*; 22,5 % *Cl*; 9,5 % *N* (=52,9 % *dipyridyl*) and 2,1 % H_2O. This product also evidently is a mixture of the *mono-dipyridyl*-compound and the *di-dipyridyl*-salt in a rather considerable quantity.

§ 4. From the foregoing results it already becomes evident, that in the presence of water, — even if a sufficient quantity of dipyridyl is present, — a partial hydrolysis of the salt *A* seems to occur, with production of the *mono-dipyridyl*-compound. Therefore, special experiments were started with the purpose of obtaining this *mono-dipyridyl*-salt in a sufficiently pure state: $Na_3\{RhCl_6\} + 12H_2O$ or $RhCl_3$, 4 *aq.* were treated, in aqueous or methylalcoholic solution, or they were finely-powdered and mixed with the molten base in the calculated (for 1 $C_{10}H_8N_2$) quantity, in a way analogous to that described in the preceding paragraph.

If 23,45 g. of $RhCl_3$, 4 *aq.*, dissolved in as little water as possible, are treated with 13 g. of dipyridyl in methylalcoholic solution, a noticeable increase of temperature in the brownish red solution is after some minutes observed and an orange-yellow, very sparely soluble precipitate is suddenly formed. The latter was filtered-off, washed with cold water and dissolved in about 2 L. of boiling water. The solution was evaporated on the water-bath and the subsequent fractions isolated, the colour of which proved to vary from orange-yellow to orange. The final fractions obtained from the last mother-liquors have the colour of the yellow salt *A*. Analysis gave i.a. the following results:

a. a brownish-coloured product yielded: 24,46 % *Rh*; 25,52 % *Cl*; 39,6 % *dipyridyl* (8,54 % *N*); and 10,4 % H_2O (4,56 % at 95° C.)

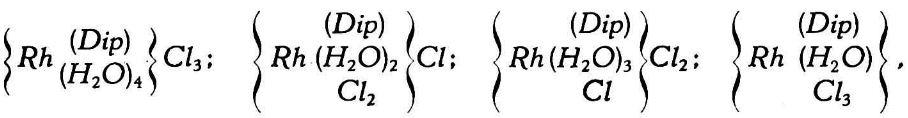
b. an orange-yellow product gave: 24,67 % *Rh*; 26,16 % *Cl*; 39,6 % *dipyridyl* (=7,16 % *N*) and 9,6 % H_2O (2,63 % at 95° C.)

c. a pale bronze-coloured fraction gave: 23,12 % *Rh*; 24,36 % *Cl*; 44,1 % *dipyridyl*; and 8,4 % H_2O (3,53 % at 95° C.)

The same experiment was executed in boiling methylalcohol as solvent. It yielded an orange-yellowish product, which was very sparely soluble and crystallized in soft scales; on analysis, they gave: 22,37 % *Rh*; 23,26 % *Cl*; 46,23 % *dipyridyl*; 7,2 % H_2O (5,3 % at 95° C.) From the mother-liquor a yellowish brown product was obtained with 21,66 % *Rh*; 22.49 % *Cl*; 47.5 % *dipyridyl* and 8,35 % H_2O (5,86 % at 95° C.).

If the experiment was repeated with molten dipyridyl and the residue was extracted with water, instead of alcohol, a brown product was obtained, yielding 24,81 % *Rh*; 25,06 % *Cl*; 7,86 % *N* (=44 % *dipyridyl*) and 6,13 % H_2O (of which 3,8 % at 95° C.). Evidently thus in all these cases principally the *mono-dipyridyl*-salt is produced, with a slight admixture of the salt *A*.

§ 5. The *mono-dipyridyl*-salts formed in these reactions possibly can have different compositions:

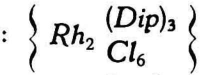


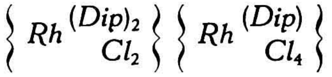
$$\left\{Rh\begin{matrix}(Dip)\\(H_2O)_4\end{matrix}\right\}Cl_3;\quad \left\{Rh\begin{matrix}(Dip)\\(H_2O)_2\\Cl_2\end{matrix}\right\}Cl;\quad \left\{Rh\begin{matrix}(Dip)\\(H_2O)_3\\Cl\end{matrix}\right\}Cl_2;\quad \left\{Rh\begin{matrix}(Dip)\\(H_2O)\\Cl_3\end{matrix}\right\},$$

and their hydrates; etc. It is rather difficult to say, which of these compounds are present in each particular case, as their spare solubility in water makes it very difficult to determine their content of ionogen chlorine. The varying results of their analysis, moreover, certainly proves that most of them are *mixtures*, which cannot be separated by recrystallisation; also the varying fraction of the total content of water, which can be eliminated at 95°—100° C., indicates that they are mixtures of differently built hydrates, while, moreover, almost in each reaction also the *di-dipyridyl*-salt is formed, which also can be separated from them with extreme difficulty. In some of the products perhaps almost 1 mol. of the *di-dipyridyl*-salt is present on 1 mol. of the *mono-dipyridyl*-salt or, at least, a compound containing 1,5 mol. of dipyridyl on 1 atom of rhodium (see below) is formed. As in the cold solution, there is originally almost *no* precipitate formed, if $AgNO_3$ is added, probably the composition of the salt is best expressed by: $\left\{ \begin{array}{c} (Dipyr) \\ Rh\,(H_2O) \\ Cl_3 \end{array} \right\} + n\,H_2O$, — in which n lies between 0,5 and 1.

As, on boiling the solution, the precipitate of $AgCl$ proves gradually to augment to 93 % of its Cl-content, a further hydrolysis at higher temperatures evidently takes place on heating the liquid, so that the composition gradually approaches to $\left\{ Rh \begin{array}{c} (Dip) \\ (H_2O)_4 \end{array} \right\} Cl_3$. In this respect it is comprehensible, that also the very bad solubility of the *mono-dipyridyl*-complexes appears to vary for the products obtained in different reactions. The quantity of ionogen chlorine of the *mono-dipyridyl*-salts in cold solution varies between 0—1,5 atoms of Cl; so that certainly the products of the reaction are mixtures of complex salts of the different types mentioned above.

§ 6. Finally an interesting experiment was made with the purpose of elucidating the behaviour of the true dipyridyl-salts of the complex rhodium-hexachloro-ion: $Na_3\{RhCl_6\} + 12H_2O$ in solution was treated with the equivalent amount of $AgNO_3$ and the salmon-coloured salt was isolated. The $Ag_3\{RhCl_6\}$ thus formed was treated with the calculated quantity of *bariumchloride* and the red solution of the bariumsalt evaporated on the waterbath. Red crystals of $Ba_3\{RhCl_6\}_2 + 7H_2O$ were obtained; then the latter were treated in *a cold solution* with the calculated quantity of *dipyridylsulphate*. After filtration, the brownish-red solution of the *dipyridyl-rhodiumhexachloride* was slowly evaporated at roomtemperature in a vacuum-exsiccator. After some days very beautiful red-brown, brilliant needles are deposited; they have the composition: $(Dipyr)_3\{RhCl_6\}_2 + 2H_2O$ and, with cold water, they give a clear brownish-red solution. If this solution, however, is repeatedly boiled with water, an orange or orange-yellow, sparely soluble precipitate is formed, which has the composition: $(Dip)_3\,Rh_2Cl_6 + 2$ à $3\,H_2O$. Analysis: 22,14 % Rh; 22,73 % Cl; 8,9 % N

(=49,6 % *dipyridyl*) and 4,93 % H_2O. The water is readily given off at 100° C. The composition, therefore, is analogous to that of the reaction-product of sodiumrhodiumchloride + 1 dipyridyl; this complex salt must, therefore, be formed from the original one by loosing $6\,HCl$ and a migration of the base into the complex ion. There is *no* ionogen chlorine present, so that its composition must be:  $\left\{ Rh_2 \begin{matrix} (Dip)_3 \\ Cl_6 \end{matrix} \right\}$ $+ 3H_2O$, — which simultaneously explains, why the water-molecules are so readily eliminated on heating at 95° C. As in some experiments the precipitate appeared to be a mixture of two differently coloured crystalline flakes, the composition mentioned occasionally could as well correspond to a mixture of *mono-* and *di-dipyridylchlororhodium*-compounds with the one formulated above, which perhaps corresponds to the structure:



$$\left\{ Rh \begin{matrix} (Dip)_2 \\ Cl_2 \end{matrix} \right\} \left\{ Rh \begin{matrix} (Dip) \\ Cl_4 \end{matrix} \right\} + 3\,H_2O.$$

Hitherto we did not succeed in separating one of the salts obtained into optically-active antipodes.

Groningen, Laboratory for Inorganic and
Physical Chemistry of the University.

Physics. — *The optical properties of the "van Leeuwenhoek" Microscope in possession of the University of Utrecht.* By P. H. VAN CITTERT. (Communicated by Prof. L. S. ORNSTEIN.)

(Communicated at the meeting of April 28, 1934.)

In order to compare the optical properties of the VAN LEEUWENHOEK-microscope of the University of Utrecht with that of other simple and compound microscopes of the 18th and 19th centuries, all microscopes in care of the University Museum of Utrecht have been brought once more in a workable condition, all lenses have been cleaned as thoroughly as possible and after these preleminaries the magnifications and the resolving powers of all instruments have been determined [1]).

As regards the determination of the resolving power, it was not possible to make use of the aperto-meter, as is usually done nowadays, because the numerical aperture gives the resolving power for those cases only in which both lenses and conditions for illumination are ideal. As soon as the lenses and the illumination are not ideal, the result of the aperto-meter method can only have the signification of an upper limit and the true

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[1]) Full particulars about the results of these measurements are to be found in "P. H. VAN CITTERT: Descriptive Catalogue of the Collection of Microscopes in charge of the University Museum of Utrecht", to be published shortly by Noordhoff, Groningen.