

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

(Communicated at the meeting of May 26, 1934).

§ 1. If to a solution of 2.76 g. crystallized ferrosulphate in water an alcoholic solution of 1.56 g. of α - α' -dipyridyl is added and the mixture evaporated on the waterbath, a dark red residu is formed, which can be dissolved in boiling methylalcohol. On slow evaporation at roomtemperature, after the small quantity of ferric hydroxide formed is removed, three fractions are obtained on fractional crystallization: 1. a dull dark stone-red salt, containing 17,35 % Fe; 29,59 % SO₄; 7,59 % N (= 42,3 % dipyridyl) and 11,76 % H₂O (7,16 % at 95° C.). The salt contains a small quantity of FeSO₄, 7 aq. and, therefore, too little dipyridyl. 2. A dark red product, containing 16,07 % Fe; 27,36 % SO₄; 42,7 % dipyridyl and 13,14 % H₂O (10,63 % at 95° C.); it contains somewhat too much dipyridyl and water. 3. A greenish black, sparely soluble or almost insoluble finely crystallized product, which also was obtained in the following experiment and which contains 15,94 % Fe; 27,65 % SO₄; 7,67 % N (= 42,8 % dipyridyl) and 13,6 % H₂O (1,54 % at 95° C.); it contains somewhat too little dipyridyl. While the red salts 1 and 2 are readily soluble in alcohol and in water, the latter salt is almost insoluble in both solvents.

As evidently hydrolysis plays an important role in the process, the experiment was repeated with a very strong solution of ferrous sulphate and a large excess of methylalcohol. Four fractions were isolated: 1. A dark red product, with 16,73 % Fe; 28,7 % SO₄; 42,1 % dipyridyl; and 12,47 % H₂O (9,92 % at 95° C.) 2. A dark red product from the mother-liquor, containing 14,0 % Fe; 23,89 % SO₄; 49,8 % dipyridyl and 12,3 % H₂O (all the water is removed at 95° C.). 3. A dark red product, precipitated by means of ether, with about 15 % Fe; 25,60 % SO₄; 49,7 % dipyridyl and 9,7 % H₂O. 4. The greenish black, insoluble, product already mentioned, having the composition indicated above.

These experiments clearly show, that salts of a perfectly constant composition are not obtained in this way: the red salts contain 2—2,5 mol. water, which for the greater part is only loosely bound; they correspond

to the formula: $\left\{ \text{Fe} \begin{matrix} (\text{Dip}) \\ (\text{SO}_4) \end{matrix} \right\} + 2 \text{ à } 2,5 \text{ H}_2\text{O}$. The insoluble, greenish-black product, however, most probably has the composition: $\left\{ \text{Fe} \begin{matrix} (\text{Dip}) \\ (\text{H}_2\text{O})_2 \end{matrix} \right\} (\text{SO}_4) + 0,5 \text{ H}_2\text{O}$; for the water is much more strongly bound and the insolubility of the product in alcohol is also in agreement with composition

indicated. In the same way the solubility of the red salts in alcohol is certainly connected with the fact, that most probably these red salts are no electrolytes, although by a continuous contact with water, they prove gradually to become hydrolysed and to be decomposed.

§ 2. Now three other experiments were started, in which 2,78 g. crystallized and finely powdered ferrous sulphate were mixed with 1,56 g., 3,12 g and 4,68 g. *dipyridyl* respectively. The mixtures were carefully heated, till the base was completely melted and then the red masses thus obtained were extracted with boiling alcohol. In all three cases a residu of ferric hydroxide was left; its weight was determined and then so much ferrous sulphate was in each case added to the solutions, as would correspond to the quantities of the hydroxide stated. The first product (1:1) was violet-brownish till brownish-red; the other two (1:2) and (1:3) were dark red. Afterwards the three products were, at room-temperature, washed with ether, with the purpose of removing some free *dipyridyl* still present, and the solutions then were evaporated in a vacuum-exsiccator at roomtemperature. Analysis yielded the following results: I. 13,76 % *Fe*; 30,09 % SO_4 ; 7,27 % *N* (= 40,5 % *dipyridyl*) and 15,66 % H_2O ; II. 9,62 % *Fe*; 22,45 % SO_4 ; 9,90 % *N* (= 55,1 % *dipyridyl*) and 12,83 % H_2O ; III. 7,66 % *Fe*; 18,46 % SO_4 ; 11,05 % *N* (= 61,54 % *dipyridyl*) and 12,34 % H_2O . Although the proportions: *Fe*: (*Dip*) here are: 1:1, 1:2 and 1:3 respectively, all three salts prove to contain a considerable excess of sulphuric acid. Evidently the sulphuric acid is, by hydrolysis, liberated from the ferrous sulphate, — so that ferric hydroxide is deposited, — and this acid then seems to react with the complex salt formed. The foregoing experiments sufficiently prove the existence of *mono*-, *di*- and *tridipyridyl*-salts of bivalent iron; but evidently these salts may all partially be decomposed by the action of the water, especially on heating their solutions. Moreover, the dry *di*- and *tri*-*dipyridyl*-salts, if heated at 100° C., prove alto to loose some *dipyridyl*. The compositions of the *pure* salts evidently are: a *mono*-*dipyridyl*salt (probably with 3 H_2O); then the salts: $\left\{ \begin{array}{l} Fe \text{ (Dip)}_2 \\ SO_4 \end{array} \right\} + 4 H_2O$, and $\{Fe(Dip)_3\} SO_4 + 5 H_2O$. But it must be remarked, that the *di*-*dipyridyl*-salt eventually may appear to be an equivalent mixture of the *mono*- and *tri*-*dipyridyl*-salts. The excess of SO_4 in all three cases proves to be about 0,062 equivalents, i.e. proportional to their contents of H_2O (1/3 equiv. for the *mono* $\frac{1}{4}$ for the *di*- and 1/5 for the *tridipyridyl*salt); evidently 1 H_2O is in all these salts substituted by 1 H_2SO_4 .

§ 3. The sulphates with 1, 2 and 3 equivalents of *dipyridyl* now were treated with the calculated quantities of $BaCl_2 + 2 H_2O$ and of $Ba(OH)_2 + 8 H_2O$, so that their excess of sulphuric acid could be caught by the latter and they thus were converted into the corresponding *chlorides*.

The filtered solutions then were evaporated at 15° C. in a vacuum. In the case of the salts with 2 and 3 equivalents of *dipyridyl*, the barium-sulphate filtered-off, proved to be coloured by admixed ferric hydroxide: in both cases, therefore, the filtered solutions certainly must contain an excess of the base. However, from all three solutions apparently the same dark red, brilliant plates were deposited, besides some *dipyridyl*. From the solution with 1 equiv. *dipyridyl* a salt was obtained, which gave: 8,46 % Fe; 10,81 % Cl; 11,22 % N (= 62,5 % *dipyridyl*) and 19,23 % H₂O. This analysis proves, that predominantly the *tridipyridyl*-salt: {Fe(Dip)₃}Cl₂ + 7 H₂O is present, in the complex ion of which, however, 0,36 equivalents of *dipyridyl* are substituted by 0,72 mol. H₂O. From the other solutions the *pure tri-dipyridyl*salt: {Fe(Dip)₃}Cl₂ + 7 H₂O was obtained in brilliant, dark red, hexagonally-shaped tables, which, on analysis, yielded: 7,70 % Fe; 9,89 % Cl; 11,49 % N (= 64,0 % *dipyridyl* and 18,40 % H₂O.

They are *rhombic-bipyramidal*, with the axial ratio: $a : b : c = 0,8886 : 1 : 0,7717$ (Fig. 1).

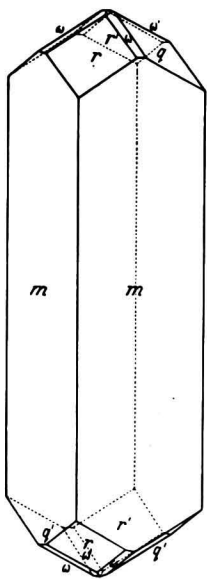


Fig. 1. *Tri-dipyridyl-Ferrochloride*

Forms observed : $m = \{110\}$, broad and very lustrous; $r = \{101\}$ and $q = \{011\}$, about equally well developed and giving good reflections; $\omega = \{112\}$, narrow and moderately well reflecting. The habitus is flattened parallel to two faces of $\{110\}$, with an elongation in the direction of the *c*-axis.

Angular values:	Measured:	Calculated:
$m : m = (110) : (\bar{1}\bar{1}0) =$	*83° 14½'	—
$m : r = (110) : (101) =$	*60 39	—
$r : q = (101) : (011) =$	53 12½	53° 17½'
$q : m = (011) : (\bar{1}\bar{1}0) =$	66 6½	66 3½
$r : \omega = (101) : (112) =$	26 36½	26 39

The crystals are only feebly dichroitic.

The products in which the *dipyridyl* is partially substituted by watermolecules, proved to have *the same* crystalforms; so that, evidently this substitution leads to salts which are completely isomorphous with the *pure tridipyridyl*salt.

The complex chlorides mentioned also were prepared, starting from ferrous chloride itself and adding 1, 2 or 3 equivalents of the base. In all these reactions the same products were obtained, as already described; only a *tridipyridyl*-salt (+ 7 H₂O) and, — in the case when 1 equivalent *dipyridyl* was added, — the compound (+ 6 H₂O), in which 0,36 mol. *dipyridyl* of the *tridipyridyl*-ferro-ion were substituted by 0,72 mol. H₂O. In the case of the *chloride*, therefore, evidently only the *tridipyridyl*-salt, in a more or less hydrolysed form, seems to exist, — in contrast with

what was stated in the case of the *sulphates*. An analogous dependance of the type of complex salts formed on the nature of the anion, as stated in the case of the ferrous salts, is, as we soon will see, also found with the corresponding salts of bivalent *copper*.

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Botany. — *Pankreas-, Speichel- und Aspergillusamylase (Taka-Diastase) als Gemisch zweier Arten von Amylasen.* Von G. GIESBERGER.
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H. P. WIJSMAN (12, 13) hat im Jahre 1889 zuerst die Existenz zweier Amylasen im Malz nachgewiesen. Er benutzte dazu eine Methode zur Trennung eines Gemisches von zwei Stoffen durch Diffusion in Gelatine-Gel.

Wenn man auf eine stärkehaltige Gelatineplatte einen Tropfen Malz-extrakt bringt, so diffundiert von dort aus die Amylase in die Gelatine und greift die Stärke an; und wenn man dann nach einer Diffusion von etwa zwei Tagen im Eisschrank die Stärke-Gelatineplatte mit einer verdünnten Lösung von Jodjodkalium behandelt, zeigt sich auf blauem Grund ein rundes Diffusionsfeld, das aus einem farblosen Zentrum besteht, welches von einem purpurnen Ringe umgeben ist.

WIJSMAN zog hieraus den Schluss, dasz sich im Malzextrakt zwei „Diastasen“ befinden müssen, welche mit verschiedener Geschwindigkeit in die Gelatine hinein diffundieren. Der purpurne Ring gibt dasjenige Gebiet an, wo nur das Enzym, welches am schnellsten in die Gelatine hinein diffundiert, auf die Stärke eingewirkt hat; wenn man nämlich aus einem nicht mit Jod behandelten Ringe ein Stück herausnimmt und dieses wieder auf eine Stärke-Gelatineplatte legt, bekommt man nur ein purpurnes Diffusionsfeld ohne farbloses Zentrum.

Mit Hilfe dieser Methode hat WIJSMAN die Eigenschaften der beiden Amylasen untersucht. Das Enzym des Ringes, die „Maltase“ (dasjenige Enzym, das wir heute im Sinne KUHN's β -Malzamyase nennen) wird durch Erhitzung zerstört. Er konnte infolgedessen die „Dextrinase“ (α -Malzamyase) durch 10 minutenlanges auf 70° C. Erhitzen herstellen. Auch durch Behandlung mit verdünnter Säure und durch fraktionnierte Alkohol-fällung konnte er die beiden Amylasen teilweise voneinander trennen. Sehr wichtig war seine Entdeckung, dasz die beiden Amylasen im Gerstenkorn an verschiedenen Stellen lokalisiert sind. Das mehliges Endosperm enthält nur β -Amylase, es war ihm daher möglich, die β -Amylase gesondert herzustellen, wobei er von geschälter Gerste ausging.