

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

(Communicated at the meeting of December 16, 1933.)

§ 1. In the course of a study of the complex α - α' -dipyridylsalts of the metals *nickel, iron, cobaltum* and *rhodium*, we observed that most of these metals were able to yield different series of such complex salts, their occurrence being dependent on the special circumstances during the preparation. In this paper we only wish to communicate some results obtained in the study of the complex salts of bivalent *nickel*.

The *tridipyridyl* salt of nickel-chloride was already described by BLAU¹⁾; this and other salts were studied more in detail by MORGAN and BURSTALL²⁾, who first succeeded in resolving the complex cation into its optically-active components. More recently, PFEIFFER and TAPPERMANN³⁾ studied the complex salts of *nickel* with α - α' -dipyridyl and *o*-phenanthroline; their results, although compatible with ours in general lines, deviate, however, from our experiences in some details which, on the other hand bring a happy completion of the facts hitherto stated.

The base used in these experiments was prepared in appreciable quantities after the method of HEIN and RETTER⁴⁾, by the interaction of anhydrous ferric chloride on pyridine in sealed tubes at 300° C. It crystallizes from ethylacetate in big, lustrous monoclinic crystals, with: $a : b : c = 0.8915 : 1 : 1.8701$ and $\beta = 85^\circ 16'$, which are limited by the forms: $\{101\}$, $\{\bar{1}01\}$ and $\{011\}$. Their meltingpoint is 71° C. The compound is volatile; its vapours have an agreeable, somewhat sweet odour.

The crystalforms of α - α' -dipyridyl are reproduced in Fig. 1¹ and 1³ for the crystals obtained from ether, in Fig. 1² and 1⁴ for those deposited from ethylacetate.

Forms observed: $s = \{\bar{1}01\}$, very lustrous, usually predominant; $r = \{101\}$, smaller than s , yielding good reflections; $q = \{011\}$, giving very sharp images and usually strongly developed.

¹⁾ F. BLAU, Monatshefte f. Chemie, **19**, (1898), 647.

²⁾ G. T. MORGAN and F. H. BURSTALL, Journ. Chem. Soc. London, (1931). II, 2213.

³⁾ P. PFEIFFER and F. TAPPERMANN, Zeits. f. anorg. Chem. **215**, (1933), 273.

⁴⁾ F. HEIN and W. RETTER, Ber. d. d. chem. Ges., **61**, (1928), 1790; conf. also: J. P. WIBAUT, Rec. Trav. Chim. Pays-Bas, **47**, (1928), 761.

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$q : q = (011) : (01\bar{1}) =^*$	$56^\circ 26'$	—
$r : s = (101) : (10\bar{1}) =^*$	50 53	—
$q : s = (011) : (\bar{1}01) =^*$	79 59	—
$q : r = (011) : (101) =$	76 39	$76^\circ 37'$

No distinct cleavability was observed.

Optically biaxial; the plane of the optical axes is $\{010\}$. On $\{\bar{1}01\}$ one of the hyperbolic branches is observed; the very strong dispersion is: $q < v$.

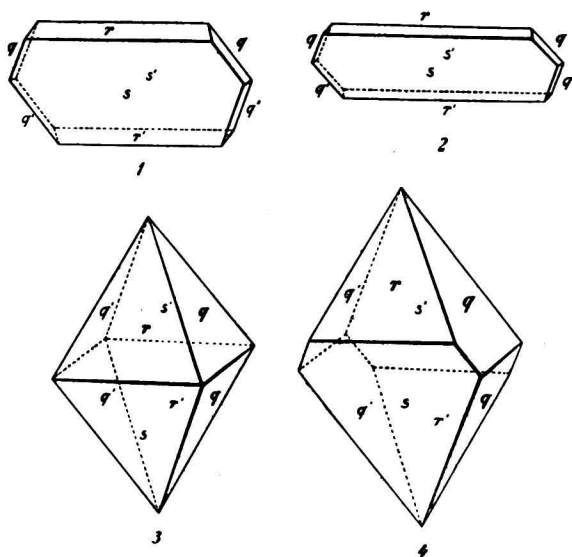
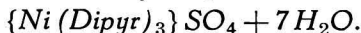


Fig. 1. *Crystalforms of α - α' -Dipyridyl.*

If a solution of 2.5 Gr *nickelsulphate* ($+ 7H_2O$) is mixed with an alcoholic solution of 4.7 Gr *dipyridyl*, the solution turns to a deep red. On evaporation on the waterbath, a red salt is obtained in beautiful monoclinic crystals, which have the composition:



Analysis: Ni: 7.80 %, calc. 7.83 %; SO_4 : 12.85 %, calc. 12.82 %; N: 11.17 %, calc. 11.22 %; H_2O : 16.8 — 17.0 %, calc. 16.81 %.

Occasionally some blue needles appeared intermixed with the red crystals. A more detailed examination taught us, that they are formed from the red salt, if an excess of *nickelsulphate* is present. If a solution of 2 equivalents of $NiSO_4 + 7H_2O$ be added to a solution of the red salt the colour of the solution, on heating on the waterbath, turns to a deep blue, and, on slow evaporation, only the blue salt is deposited from it in needles which have the aspect of *coppersulphate*. The same salt is also produced,

if a solution of nickelsulphate is mixed with an alcoholic solution of 1 equivalent of dipyridyl: the solution turns red during a very short interval of time, then rapidly gets blue and on evaporation the same blue needles as mentioned are deposited on cooling. They are triclinic, only sparingly soluble in cold, better in hot water; they have the composition: $\left\{ \begin{array}{l} Ni \text{ (Dipyrr)} \\ (H_2O)_2 \end{array} \right\} SO_4 + 4 H_2O$. At $100^\circ C$. only $4 H_2O$ are expelled, but not the two water-molecules of the complex ion.

Analysis: Ni: 13.96 %, calc. 14.01 %; SO_4 : 22.5 %, calc. 22.93 %; N: 6.67 %, calc. 6.68 %; H_2O : 16.85 %, calc. 17.2 %.

If the crystallized, finely pulverized nickelsulphate (+ $7 H_2O$) is added to a concentrated solution of the red tridipyridylsalt, (2 equiv. of the sulphate + 1 equiv. of the red salt) and the mixture, under continually stirring, be heated on the waterbath, the solution turns to a deep indigo-blue colour; on cooling, an aggregate of long, pale blue, hair-like needles is deposited, which have the same composition as the blue needles previously mentioned. They evidently represent a second modification of the blue salt; after dissolving them in water, they yield a pale blue solution, from which the ordinary triclinic needles are once more deposited.

§ 2. *Tridipyridylnickelsulphate* (+ $7 H_2O$) crystallizes in deep pink, monoclinic crystals (Fig. 2). They are very lustrous, hard and well developed; in most cases they have the aspect of thick plates (Fig. 2A), sometimes of rectangular flattened crystals. (Fig. 2B).

Monoclinic-prismatic.

$$a : b : c = 1.5342 : 1 : 0.9134 ; \beta = 82^\circ 19\frac{1}{2}'$$

Forms observed: $a = \{100\}$, either small or predominant, always yielding very sharp reflections; $m = \{110\}$, very lustrous; $r = \{\bar{1}01\}$, often strongly predominant and always broader than $s = \{101\}$; both forms give very good reflections.

Moreover, $q = \{011\}$, small and yielding dull images.

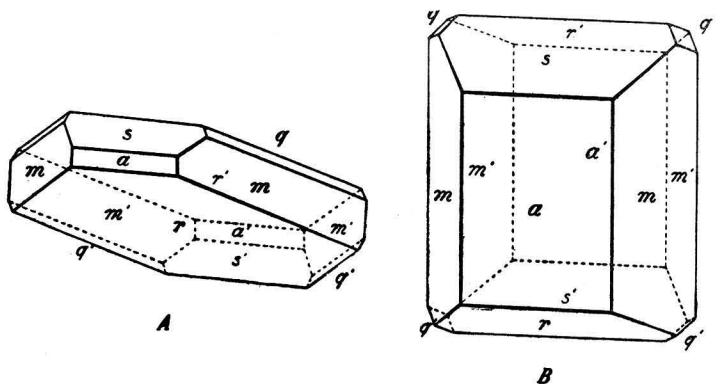


Fig. 2. Crystalform of Tridipyridyl-Nickelsulphate (+ $7 H_2O$).

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$a : m = (100) : (110) =^*$	56° 40'	—
$r : s = (\bar{1}01) : (101) =^*$	61 19	—
$a : r = (100) : (10\bar{1}) =^*$	65 1	—
$m : q = (110) : (011) =$	52 6	52° 31½'
$r : q = (\bar{1}01) : (011) =$	51 19	51 22½'
$m : q = (110) : (0\bar{1}1) =$	59 32	59 35
$m : s = (\bar{1}10) : (101) =$	71 8	71 0
$m : r = (110) : (10\bar{1}) =$	76 35	76 35
$a : s = (100) : (101) =$	53 40	53 40
$m : m = (110) : (\bar{1}10) =$	66 40	66 40
$s : q = (\bar{1}0\bar{1}) : (01\bar{1}) =$	49 20	49 25

No distinct cleavability was observed.

The optical axial plane is {010}; inclined dispersion. On {100} the crystals are strongly dichroitic: for vibrations parallel to the *c*-axis pale-red, for such parallel to the *b*-axis blood-red. One of the optical axes emerges on {100} almost perpendicularly to this plane.

The salt is a derivative of a moderately strong complex cation. On heating with strong nitric acid or aqua regia, it is decomposed; but as long as dipyriddy is present in the solution, the complex ion afterwards is regenerated and the solution, on evaporation, again turns red. For the purpose of analysis the salt was destructed by carefully melting it with soda and sodiumnitrate. Ammonia yields no precipitate in the solution of the salt, not even at boiling-temperature, sodiumhydroxide at room-temperature gives a slight precipitate; on boiling, dipyriddy is set free, but the greenish solution later-on again gets colourless. Strong nitric acid (1.30) does not attack the substance at room-temperature; on boiling, the liquor gets blue and, on cooling, violet. Strong hydrochloric acid behaves in an analogous way, the solution, on boiling, assuming a green colour, which, on cooling, turns to blue or bluish-violet. Aqua regia renders the solution colourless; later-on it gets green. A solution of bromine in water yields a yellow or orange precipitate, on heating, the solution turns a pale-pink and a reddish precipitate is formed.

On heating with a strong solution of yellow ammoniumsulphide, a black precipitate of *NiS* is slowly formed, but the decomposition is incomplete and can only be performed by repeatedly heating of the substance with an excess of fresh ammoniumsulphide-solution.

§ 3. *Monodipyridyl-diaquo-nickelsulphate* (+ 4 H_2O) crystallizes

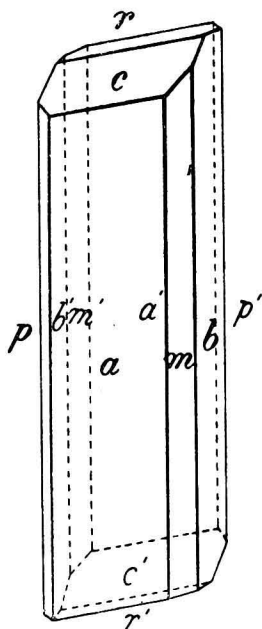


Fig. 3. Crystal form of *Monodipyridyl-diaquo-Nickelsulphate* (+4 H_2O).

from its pale-blue solutions in beautiful, blue needles. The crystals are triclinic, long prisms with a flattening parallel to $\{010\}$; this form shows a very fine vertical striation. Also $\{100\}$ has such a striation parallel to the c -axis; doubtlessly the crystals possess a polysynthetic lamellar structure parallel to $\{100\}$ and $\{010\}$. In the zone of the c -axis the angular values, because of the occurrence of vicinal faces, often oscillate within wider limits.

Triclinic-pinacoïdal.

$$a : b : c = 1.8786 : 1 : 1.2179.$$

$$A = 75^\circ 58' ; \quad a = 75^\circ 58'$$

$$B = 127 \quad 54 ; \quad \beta = 127 \quad 54$$

$$C = 58 \quad 2 ; \quad \gamma = 94 \quad 58$$

Forms observed: $a = \{100\}$, smooth, well reflecting, often vertically striated; $b = \{010\}$ broader than a , always finely striated, yielding coloured or multiple, somewhat dull reflections, $c = \{001\}$, well developed, very lustrous and, like $r = \{\bar{1}01\}$, giving sharp reflections; $m = \{110\}$, narrow, sometimes equally broad as a ; $p = \{\bar{1}\bar{1}0\}$, very narrow, often absent. The habitus is long-prismatic in the direction of the c -axis. (Fig. 3.)

Angular Values:

Observed: Calculated:

$a : b = (100) : (010) =^*$	94° 58'	—
$b : c = (0\bar{1}0) : (001) =^*$	104 2	—
$c : a = (001) : (100) =^*$	52 6	—
$c : r = (001) : (\bar{1}01) =^*$	39 8	—
$m : a = (110) : (100) =^*$	60 19	—
$m : b = (110) : (010) =$	34 39	34° 39'
$b : p = (0\bar{1}0) : (\bar{1}\bar{1}0) =$	31 37	31 44
$p : a = (\bar{1}\bar{1}0) : (100) =$	53 25	53 18
$r : a = (\bar{1}01) : (\bar{1}00) =$	88 46	88 46
$b : r = (010) : (\bar{1}01) =$	76 39	76 8

No distinct cleavability was observed.

The optical extinction on all faces of the vertical zone is oblique to the

boundaries of the different planes: on {010} it makes an angle of about 42° with respect to the *c*-axis.

The crystals are dichroïtic: on {010} pale-blue and dark-blue; on {100} bluish-white and pale-blue. On {010} one of the optical axes emerges at the border of the image; one axis is almost perpendicular to {110}, and a conical refraction is observed. The axial plane is inclined at about 42° with respect to the *c*-axis. The dispersion is appreciable.

§ 4. Tentatives were also made with the purpose of preparing a salt with 2 molecules of dipyrïdyl in the complex cation. Two equivalents of the red salt in solution were, therefore, mixed with a solution of 1 equivalent of $NiSO_4 + 7H_2O$. A reddish-violet solution thus was obtained, from which, however, on slow evaporation only crystals of the red and the blue salts besides each other were deposited. Also on mixing a solution of the blue salt with an alcoholic solution of 1 equivalent of dipyrïdyl, only a mixture of the blue salt and the dipyrïdyl in excess could be obtained.

Evidently, therefore, it is impossible in aqueous solutions to obtain a salt of the type: $\{Ni (Dip)_2\} X_2$. This experience is in accordance with that of PFEIFFER and TAPPERMANN¹⁾, who also were unable to obtain a salt of the composition: $\{Ni (Dipyr)_2\} X_2$ from aqueous solutions. However, they prepared a *green* salt: $\{Ni (Dipyr)_2\} Cl_2$ by carefully heating the previously dehydrated *tridipyrïdyl*-salt: one molecule of the base then is expelled and the green salt of the said composition is formed. This, however, proved to be unstable in aqueous solution, the red tridipyrïdyl-salt then being regenerated.

A similar reaction is produced, when the blue solution of the salt: $\left\{ Ni \begin{matrix} (Dipyr) \\ (H_2O)_2 \end{matrix} \right\} SO_4 + 4H_2O$ at room-temperature is treated with the right quantity of bariumhydroxide: a greenish, colloidal precipitate is produced and the colour of the solution once more gets red. Evidently the reaction: $3 \left\{ Ni \begin{matrix} (Dipyr) \\ (H_2O)_2 \end{matrix} \right\} SO_4 + 4H_2O + 3Ba(OH)_2 = \{Ni(Dipyr)_3\} (OH)_2 + 2Ni(OH)_2 + 3BaSO_4 + 18H_2O$ takes place, the precipitate formed being a mixture of bariumsulphate and nickelhydroxide.

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¹⁾ loco cit., p. 277.