

Chemistry. — *On Some Complex Dipyriddy-Salts of Nickel and Copper.*
By F. M. JAEGER and J. A. VAN DIJK.

(Communicated at the meeting of October 26, 1935).

§ 1. As a completion of the data previously published¹⁾ about the complex salts of *dipyriddy* and bivalent *nickel*, we here give a review of the results obtained in the study of the interaction of the base mentioned with *nickel nitrate* and *nickel chloride*. At the same time a correction of the crystallographical data²⁾ concerning *tridipyriddy-copper chloride* (+ 7 H₂O) is inserted at the end of this paper.

§ 2. *Nickel nitrate*. If to a solution of *nickel nitrate* one, two or three equivalents of *dipyriddy* respectively are added, these solutions on slow evaporation at room-temperature all in the first instance will deposit a red salt, which on analysis proves to be a *tridipyriddy-nickel nitrate* of the composition³⁾: {Ni (Dipyr)₃} (NO₃)₂ + 5 H₂O; analysis yielded: 7.87 % Ni; 12.00 % H₂O and 15.20 % N; calculated: 7.92 % Ni; 12.15 % H₂O and 15.12 % N.

The compound: {Ni (Dipyr)₃} (NO₃)₂ + 5 H₂O crystallizes from its concentrated aqueous solutions at room-temperature in the shape of red, elongated tables. The crystals are badly built; all occurring faces, except those of the basis, are striated parallel to the basal plane and yield very bad, multiple reflections.

The crystals are optically uniaxial; the double refraction is positive.

Hexagonal (di-)bipyramidal.

$$a : c = 1 : 0.802.$$

Forms observed : $c = \{0001\}$, lustrous and ordinarily well reflecting; $p = \{20\bar{2}1\}$, broader than $m = \{1010\}$, both yielding

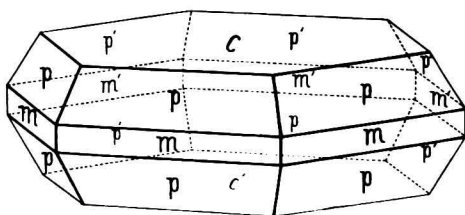


Fig. 1. *Tri-dipyriddy-Nickel nitrate* (+ 5 H₂O). very dull reflections; in some cases $\omega = \{10\bar{1}1\}$ was indicated, but extremely small.

¹⁾ F. M. JAEGER and J. A. VAN DIJK, these Proceedings, 37, (1934), 10.

²⁾ Ibidem, 37, (1934), 399, 400.

³⁾ P. PFEIFFER and K. QUEHL give 6 H₂O, Berl. Ber. 64, (1931), 2667, etc.; cf. also: Zeits. f. Anorg. Chemie, 215, (1933), 278. We never found more than 5 H₂O.

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i> (from spectrogr. data)
$c : p = (0001) : (20\bar{2}1) = *$	$60^\circ 19' - 61^\circ 40'$	$61^\circ 38'$
$p : m = (20\bar{2}1) : (10\bar{1}1) =$	$29\ 41 - 28\ 20$	$28^\circ 22'$
$c : \omega = (0001) : (10\bar{1}1) =$	$43^\circ - 48^\circ$ (estimated)	$47^\circ 43'$

From oscillation-spectrograms round [0001] (*Fe- α* -radiation), the dimensions of the elementary cell were found to be: $a_0 = 13.5$ A.U. and $c_0 = 10.8$ A.U.; from a LAUE-pattern on {0001} the dihexagonal symmetry could be deduced with a fair probability. The cell contains two molecules of the salt; d (calculated) = 1,435; value observed: 1,46.

§ 3. From the solution with 2 equivalents of dipyridyl, after deposition of some tridipyridyl-salt, pale violet prisms or needles are obtained, which in most cases form intergrowths and clusters of crystals. Because their angular values oscillate within rather wide limits, they can only be measured with difficulty; thus for instance their vertical zone is rather badly built and shows vicinal forms. Analysis yielded: 10.85 % Ni; 22.53 % (NO_3); 15.12 % N. The salt is the *di*-dipyridyl-salt of the composition: $\{\text{Ni}(\text{Dipyr})_2\}(\text{NO}_3)_2 + 3\text{H}_2\text{O}$; theoretically: 10.69 % Ni; 22.59 % (NO_3); and 15.3 % N.

Monoclinic-prismatic.

$$a : b : c = 0.3912 : 1 : 0.3825; \beta = 73^\circ 43'.$$

Forms observed: $a = \{100\}$, mostly predominant; $m = \{110\}$, narrow, well reflecting; $p = \{210\}$ and $s = \{610\}$, both very narrow and yielding

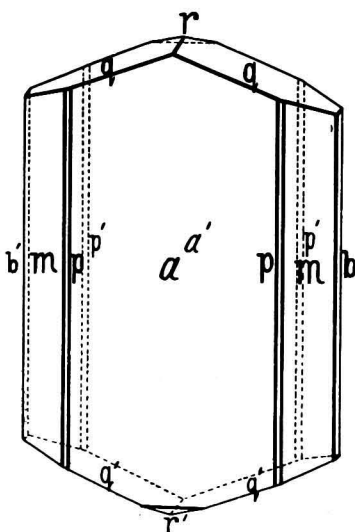


Fig. 2. *Di-dipyridyl-Nickel nitrate* (+ 3 H_2O).

bad reflections; $b = \{010\}$, extremely narrow, reflecting better than s and p ; $q = \{011\}$, yielding good reflections; $r = \{\bar{4}03\}$, small and dull. The habitus is flat prismatic (Fig. 2).

Angular Values:	Observed:	Calculated:
$a : m = (100) : (110) =^* 20^\circ 35'$		—
$q : q = (011) : (0\bar{1}1) =^* 40 18$		—
$m : q = (110) : (011) =^* 68 27$		—
$r : q = (\bar{4}03) : (011) = 64^\circ - 65^\circ$		$64^\circ 52\frac{1}{2}'$
$m : p = (110) : (210) = 8^\circ - 9^\circ$		9 57
$p : s = (210) : (610) = \text{ca. } 7^\circ$		6 38
$s : a = (610) : (100) = \text{ca. } 3\frac{1}{2}^\circ$		4 0
$b : m = (010) : (110) = 69 25$		69 25
$m : m = (110) : (\bar{1}10) = 138 50$		138 50
$b : q = (010) : (011) = 69 51$		69 51
$m : r = (\bar{1}10) : (\bar{4}03) = \text{ca. } 47^\circ$		46 57

The crystals are very brittle, but no distinct cleavage was observed. The optical axial plane is horizontal; on a normal extinction. The crystals are strongly dichroïtic: on $\{100\}$ for vibrations parallel to the c -axis pale pink, for those perpendicular to these, blue.

§ 4. From the solution with 1 equivalent of dipyrïdyl, which originally assumes a lilac-red colour, but gradually turns a dark blue, first some red crystals of the *tridipyrïdyl*-salt are deposited. Later on blue crystals appear. On analysis they proved to yield: 14.81 % Ni ; 13.89 % N and 30.91 % (NO_3). Although they evidently are not yet quite pure, there can be no doubt that they represent the *monodipyrïdyl*-salt of the composition:

$\left\{ Ni \begin{matrix} (Dipyr) \\ (H_2O)_2 \end{matrix} \right\} (NO_3)_2 + H_2O$, which requires: 14.94 % Ni ; 14.26 % N and 31.57 % (NO_3).

Hitherto this compound could not be obtained in the form of measurable crystals.

Nickel nitrate: $Ni(NO_3)_2 + 6H_2O$, therefore, proves to be able of generating all 3 types of complex dipyrïdyl-salts.

§ 5. *Nickel chloride*. From the aqueous solutions with 3 or 2 equivalents of the base we hitherto could isolate only the *tridipyrïdyl*-salt in beautiful, flat, dark red crystals of the composition: $\{Ni (Dipyr)_3\} Cl_2 + 7H_2O$; analysis yielded the following results: Ni : 8.10 %; N : 11.51 %;

H_2O at 100° C.) : 17.3 %; theoretically: Ni: 8.11 %; N: 11.61 %; H_2O : 17.4 %.

The crystals have the shape of thick parallelograms or of elongated, hexagonally bordered needles. They are soft and easily deformable.

Monoclinic-prismatic.

$$a : b : c = 0.6113 : 1 : 2.0981 ; \beta = 72^\circ 55\frac{1}{2}'.$$

Forms observed: $c = \{001\}$, predominant, very lustrous and yielding excellent reflections; $m = \{110\}$, broad and giving sharp images; $q = \{011\}$, well developed, yielding good reflections; $o = \{112\}$, always

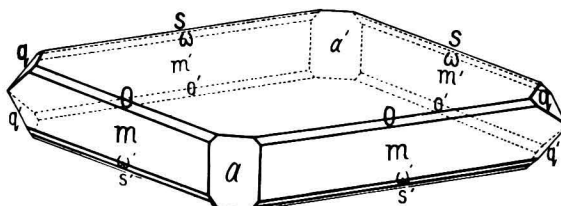


Fig. 3. *Tri-dipyridyl-Nickel chloride* (+ 7 H_2O).

present, narrow, well measurable; $a = \{100\}$, narrow, often absent, but if present, yielding weak but good reflections; $\omega = \{\bar{1}12\}$ and $s = \{\bar{1}14\}$, narrow, well measurable, ω ordinarily broader than s . The habitus is tabular parallel to $\{001\}$, either somewhat elongated parallel to the b -axis or, rarely, parallel to the a -axis.

Angular Values:	Observed:	Calculated:
$c : m = (001) : (110) =^*$	$75^\circ 19'$	—
$c : q = (001) : (011) =^*$	$63 \quad 30$	—
$a : m = (100) : (110) =^*$	$30 \quad 18$	—
$c : o = (001) : (112) =$	$51 \quad 41$	$51^\circ 57\frac{1}{3}'$
$o : m = (112) : (110) =$	$23 \quad 18$	$23 \quad 21\frac{2}{3}$
$m : \omega = (110) : (1\bar{1}2) =$	$28 \quad 58$	$29 \quad 8$
$\omega : s = (1\bar{1}2) : (1\bar{1}4) =$	$23 \quad 30$	$23 \quad 26\frac{1}{3}$
$c' : s = (00\bar{1}) : (1\bar{1}4) =$	$52 \quad 0$	$52 \quad 6\frac{2}{3}$
$m : q = (110) : (012) =$	$55 \quad 42$	$55 \quad 37\frac{1}{2}$

Imperfectly cleavable parallel to $\{001\}$.

1) The water content (7 H_2O) is in perfect accordance with the isomorphism of this salt with corresponding zinc- and copper-salts. In the literature (G. T. MORGAN and F. H. BURSTALL, Journ. Chem. Soc. London, (1931), 2213) is given: 6 H_2O ; but the salt loses over P_4O_{10} only 6 molecules of water, the seventh however at 100° C.

The crystals are feebly dichroitic: for vibrations parallel to {010} on {001} paler red than for those parallel to the *b*-axis. The axial plane is perpendicular to {010}; on {001} two axial images at the border of the field and no exactly determinable extinction. The first bisectrix is almost perpendicular to {001}.

The crystals are isomorphous with the corresponding *zinc*- and *copper*-salts.

By heating of the tridipyridyl-salt, a loss of 38.62 % was observed; this corresponds (38.97 %) to (1 *Dipyridyl* + 7H₂O). The product generated is the anhydrous *di-dipyridyl*-salt of PFEIFFER and TAPPERMANN¹), which is not stable in solutions. If brought into water, its colour changes to a dark blue and it then dissolves to a blue or lilac solution, which gradually assumes a redder hue, finally giving the red *tri-dipyridyl*-salt.

§ 6. From a solution of *nickel chloride* with 1 equivalent of dipyridyl, a solution was obtained which originally had a reddish blue colour, turning rather dark blue after some time. After a primary deposition of the red *tri-dipyridyl*-salt, the colour of the solution turns a still darker blue and finally it deposits *green* crystals, which on analysis proved to be an impure *monodipyridyl*-salt: 15.61 % Ni; 18.5 % Cl; 9.23 % N and 12.42 % H₂O. The last mother-liquor is dark green: from it a dull green, crystallized product was obtained, which proved to be the nearly pure salt: $\left\{ \begin{array}{l} Ni \\ (H_2O)_2 \end{array} \right\} Cl_2$, as the analysis yielded: 17.74 % Ni; 21.77 % Cl; 8.58 % N and 12.89 % H₂O; theoretically: 18.2 % Ni; 22.0 % Cl; 8.71 % N and 11.20 % H₂O. The salt is highly hygroscopic.

Evidently, in aqueous solutions, only the *mono*- and *tri-dipyridyl*-salts are stable; the former, however, has a tendency to change into the latter under the influence of the solvent.

§ 7. *Tridipyridyl-Copper chloride*: {Cu (*Dipyr*)₃ Cl₂ + 7H₂O} was formerly described as *rhombic*. A closer examination of some better developed crystals has, however, shown that the crystals are geometrically and optically pseudo-rhombic, in reality *monoclinic-prismatic*, just as the *zinc*- and *nickel*-salts.

Axial ratio:

$$a : b : c = 0.6114 : 1 : 2.1278; \quad \beta = 72^\circ 54\frac{1}{2}'.$$

The violet, hexagonally bounded, flat crystals show the following forms: *c* = {001}, very lustrous and predominant; *m* = {110}, well developed, yielding good images; *q* = {011}, narrow, often striated parallel to the *a*-axis, giving dull reflections; *b* = {010}, often absent, but otherwise

¹) P. PFEIFFER and F. TAPPERMANN, Zeits. f. Anorg. Chemie, 215, (1933), 277.

broader than q ; $o = \{11\bar{2}\}$, very narrow, weakly reflecting like $\omega = \{11\bar{4}\}$ and $s = \{11\bar{2}\}$, which are often absent.

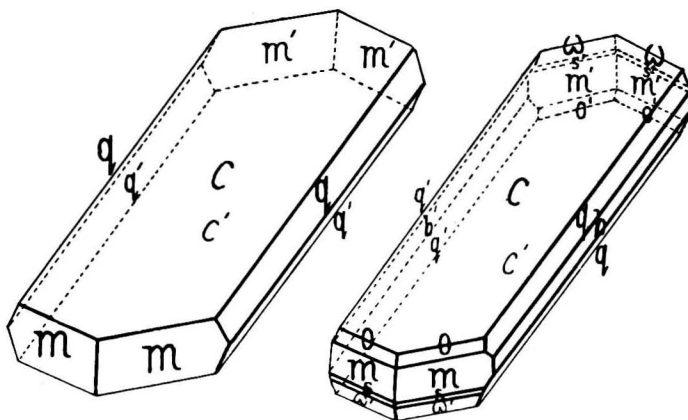


Fig. 4. *Tri-dipyridyl-Copper chloride (+ 7 H₂O).*

Angular Values:	Observed:	Calculated:
$c : m = (001) : (110) = ^* 75^\circ 18'$		—
$c : q = (001) : (011) = ^* 63 \quad 49$		—
$m : m = (110) : (1\bar{1}0) = ^* 60 \quad 36$		—
$q : b = (011) : (010) = 26 \quad 11$		$26^\circ 11'$
$c : o = (001) : (112) = 52 \quad 20$		$52 \quad 9$
$o : m = (112) : (110) = 23 \quad 34\frac{1}{2}$		$23 \quad 45\frac{1}{2}$
$b : m = (010) : (110) = 59 \quad 42$		$59 \quad 42$
$\omega : c' = (11\bar{4}) : (00\bar{1}) = 52 \quad 40$		$52 \quad 38$
$m : q = (011) : (110) = 55 \quad 39$		$55 \quad 48$
$m : s = (110) : (11\bar{2}) = 28 \quad 40$		$28 \quad 34$
$s : \omega = (11\bar{2}) : (11\bar{4}) = 23 \quad 17$		$23 \quad 12$

No distinct cleavability was observed.

The crystals are upon $\{001\}$ only weakly dichroitic, but very strongly on $\{010\}$: for vibrations parallel to the a -axis violet blue, for such parallel to the c -axis, bluish green. The plane of the optical axes is perpendicular to $\{010\}$; the first bisectrix is practically perpendicular to $\{001\}$. The apparent optical angle is only small.

All these salts: *nickel-*, *zinc-* and *copper-*salts are pseudo-rhombic, which is clearly shown when m is taken as $\{111\}$ and $a = \{101\}$: then the angle β is very close to 90° ; also in their optical behaviour they betray this approximation to rhombic symmetry.

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