

Ein Potenzprodukt  $P = g^{p_1} A_{22}^{p_2} D^{p_3}$  gibt bei  $C$  nach (2) und wegen  $C(D) = 0$

$$C(P) = (-p_1 - 2p_2) \cdot P;$$

bei absoluten  $C$ -Invarianten muss also  $-p_1 - 2p_2 = 0$  sein, d.h.  $p_1 = p_2 = 0$ . Der fünfte und letzte Schritt liefert demnach als Integritätsbasis für die absoluten  $C$ -Invarianten  $K$ :

$$(K) = \varphi, D,$$

womit auch die Basis für die Komitanten ermittelt ist.

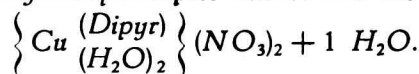
**Chemistry — On Complex Salts of  $\alpha$ - $\alpha'$ -Dipyridyl with Bivalent Copper. II.** By F. M. JAEGER and J. A. VAN DIJK.

(Communicated at the meeting of October 27, 1934).

§ 1. In previous papers on complex salts of  $\alpha$ - $\alpha'$ -dipyridyl and bivalent metals<sup>1)</sup> we have drawn attention to the fact that the number of molecules of the base introduced into the complex ion evidently is often dependent on the special nature of the anion of the metallic compounds used in the reaction. Especially in the case of the ferrous salts — sulphates and chlorides — and in that of the cupric chloride and sulphate this fact was stated beyond all doubt. As a further proof of the correctness of this view, we here communicate the results obtained in the reaction between  $\alpha$ - $\alpha'$ -dipyridyl and copper *nitrate*.

If to a solution of copper nitrate in water an alcoholic solution of 1, 2 or 3 equivalents of dipyridyl is added, the colour of the solutions turns in all three cases to a deep blue. On slow evaporation, dark blue crystals of the *tri*- and *di*-dipyridyl-salts are soon deposited: in contrast to what was observed of the cupric salts previously described, the solution of the *mono*-dipyridyl salt does not easily crystallize and proves to contain the most soluble compound of the three; finally, however, also from this solution a dark blue salt is deposited, which is a true *mono*-dipyridyl-cupric nitrate. Cupric nitrate, therefore, readily forms complex salts with dipyridyl, corresponding to all three types mentioned.

§ 2. *Mono-dipyridyl-diaquo-cupric nitrate* has the composition:



The salt crystallizes in aggregates of thick tabular crystals or in separate, smaller, needle-shaped crystals of a dark blue colour; they are distinctly dichroïtic. Analysis: 16.04% Cu; 13.38%  $\text{H}_2\text{O}$ ; theoretically: 15.98% Cu and 13.59%  $\text{H}_2\text{O}$ . Evidently the salt has a composition analogous

<sup>1)</sup> F. M. JAEGER and J. A. VAN DIJK, *Proceed. R. Acad. Sciences Amsterdam*, 37 (1934), 10, 333; 395.

to the following, — one molecule dipyriddy in it being substituted by two molecules of water.

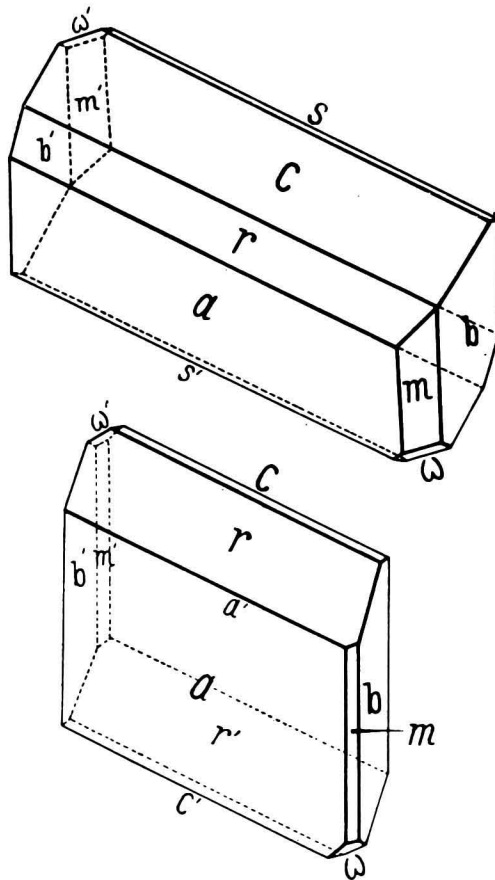
The crystals are triclinic-pinacoidal; their axial ratio is:  $a:b:c = 1.4411:1:0.7766$ , with:

$$A = 91^{\circ} 23'; \alpha = 101^{\circ} 56'$$

$$B = 105 51; \beta = 109 42$$

$$C = 58 2; \gamma = 56 8$$

*Forms observed:*  $a = \{100\}$ , predominant and lustrous;  $b = \{010\}$ , very lustrous and well developed;  $c = \{001\}$ , mostly rather broad and lustrous, sometimes, however, very narrow;  $r = \{101\}$ , broad and very lustrous;  $m = \{110\}$ , well developed and yielding good reflections, but less brilliant than  $a$  or  $c$ ;  $\omega = \{\bar{1}\bar{1}1\}$ , small but well reflecting, with more or less oscillating angular values;  $s = \{10\bar{1}\}$ , extremely narrow, only approximately measurable, often absent. The habitus is elongated parallel to the  $b$ -axis and either tabular or needle-shaped. (Fig. 1).

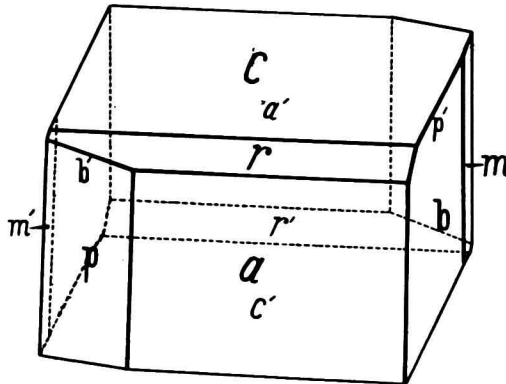


*Fig. 1. Crystal form of Monodipyriddy-Cupric-Nitrate (+ H<sub>2</sub>O)*

<i>Angular Values:</i>	<i>Observed Calculated:</i>		
$a : c = (100) : (001) =^* 74^\circ$	9'	—	
$a : b' = (100) : (0\bar{1}0) =^* 58$	2	—	
$c : b' = (001) : (0\bar{1}0) =^* 91$	23	—	
$a : m = (100) : (110) =^* 77$	16	—	
$a : r = (100) : (101) =^* 46$	39	—	
$m : b = (110) : (010) =$	44	42	$44^\circ 42'$
$r : c = (101) : (001) =$	27	30	27 30
$c : m = (001) : (110) =$	75	14	75 17
$a' : \omega' = (\bar{1}00) : (\bar{1}\bar{1}1) =$	95	30	95 28
$b' : r = (0\bar{1}0) : (101) =$	76	18	76 20
$\omega : c = (\bar{1}\bar{1}1) : (001) =$	42	18	42 37
$a' : s = (\bar{1}00) : (\bar{1}01) =$	ca	$69^\circ$	69 33
$c : s = (001) : (\bar{1}01) =$	ca	$37^\circ$	36 28
$b' : \omega = (0\bar{1}0) : (\bar{1}\bar{1}1) =$	ca	$61^\circ.5$	61 36
$m : \omega' = (110) : (1\bar{1}\bar{1}) =$	ca	$61^\circ.5$	62 6

No distinct cleavability was observed. On  $\{100\}$  oblique extinction, at about  $44^\circ$  with the edge  $a : r$ . Dichroitic; on  $\{100\}$ , for vibrations in a direction including  $45^\circ$  with  $a : r$ , dark blue; for such perpendicular to those, pale blue.

§ 3. *Didipyridyl-Cupric-nitrate* has the composition:  $\{Cu (Dipyr)_2\} (NO_3)_2 + 1 H_2O$ ; the analysis gave:  $Cu : 12.21\%$ ;  $H_2O : 3.37\%$ ; calculated:  $12.27\%$   $Cu$  and  $3.48\%$   $H_2O$ . The salt is less soluble than the previous one. From water it crystallizes at room-temperature in thick, not very perfectly built crystals. They are triclinic, but represent pseudo-monoclinic limiting forms.



*Fig. 2. Crystal form of Didipyridyl-Cupric-Nitrate (+1H<sub>2</sub>O)*

*Triclinic-pinacoidal (pseudo-monoclinic)*

$$a : b : c = 2.0562 : 1 : 1.3385;$$

$$A = 90^\circ 38'; \alpha = 90^\circ 13'$$

$$B = 111 \ 52; \beta = 111 \ 51\frac{1}{3}$$

$$C = 91 \ 9; \gamma = 90 \ 59$$

*Forms observed*:  $a = \{100\}$  and  $c = \{001\}$ , both very well developed, very lustrous, but often yielding multiple reflections;  $b = \{010\}$ , broad and very lustrous;  $r = \{101\}$ , well developed and giving good images;  $m = \{1\bar{1}0\}$ , very lustrous, mostly narrow; sometimes a curved, rough face  $\{10 \cdot \bar{1} \cdot 0\}$  occurs as a vicinal form and also a very small vicinal form  $\{11 \cdot 0 \cdot 1\}$ . The habitus is short or thickly prismatic, with an elongation parallel to the  $b$ -axis. (Fig. 2).

*Angular Values: Observed: Calculated:*

$a : c = (100) : (001) =^*$	68°	8'	—
$a : b = (100) : (010) =^*$	88	51	—
$b : c = (010) : (001) =^*$	89	22	—
$a : m = (100) : (1\bar{1}0) =^*$	63	15	—
$a : r = (100) : (101) =^*$	42	12	—
$m : r = (1\bar{1}0) : (101) =$	70	46	70° 40'
$b : r = (010) : (101) =$	88	49	89 0
$m : b' = (1\bar{1}0) : (0\bar{1}0) =$	27	54	27 44
$c : r = (001) : (101) =$	25	56	25 56

No distinct cleavability was observed.

On  $\{001\}$  for vibrations almost perpendicular to the edge  $a : c$ , the colour is dark blue, for such at right angles with those, greenish blue; this dichroïsm is only weak. The extinction on  $\{100\}$  and  $\{001\}$  is oblique, under a very small angle ( $4^\circ$  or  $5^\circ$ ) with respect to the edge  $a : c$ .

§ 4. *Tridipyridyl-Cupric Nitrate*:  $\{Cu(Dipyr)_3\}(NO_3)_2 + 6H_2O$  is deposited from its aqueous solution in the shape of hexagonally bordered, flat, dark blue crystals. They are very plastic, because of the presence of gliding planes; their edges are often rounded and their angular values are rather variable. Analysis yielded:  $Cu : 8.33\%$ ;  $H_2O : 14.10\%$ ;  $N : 15.09\%$ , theoretically:  $8.33\%$   $Cu$ ;  $14.15\%$   $H_2O$ ;  $14.7\%$   $N$ .

*Monoclinic-prismatic.*

$$a : b : c = 1,6577 : 1 : 1,4960.$$

$$\beta = 87^\circ 0'.$$

*Forms observed*:  $c = \{001\}$ , predominant, yielding very sharp images;  $a = \{100\}$ , dull, mostly horizontally striated;  $\omega = \{111\}$  and  $o = \{\bar{1}\bar{1}1\}$ ,

almost equally broad and giving good reflections;  $m = \{110\}$ , only small and narrow, moderately reflecting. The habitus is tabular parallel to

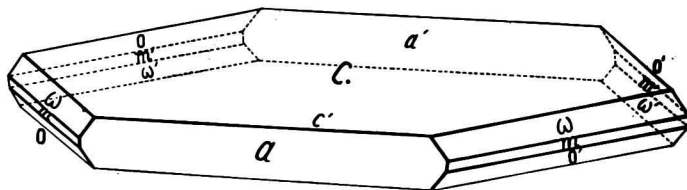


Fig. 3. Crystalform of Tridipyridyl-Cupric-Nitrate(+6H<sub>2</sub>O)

$\{001\}$ , with a slight elongation in the direction of the  $b$ -axis. The salt is less soluble than the *di*-dipyridyl salt just described.

Angular Values:                      Observed: Calculated:

$a : c = (100) : (001) =^*$	87°	0'	—
$c : o = (001) : (\bar{1}11) =^*$	62	50	—
$o : o = (\bar{1}11) : (111) =^*$	80	45	—
$c : \omega = (001) : (111) =$	60	45	60° 36'
$o : \omega = (\bar{1}11) : (111) =$	50	40	50 12½'
$\omega : m = (111) : (110) =$	27	43	27 51
$o : m = (111) : (110) =$	28	51	28 43
$a' : o = (\bar{1}00) : (\bar{1}11) =$	66	4	66 23½'
$a : \omega = (100) : (111) =$	63	16	63 24

Cleavable parallel to  $\{001\}$ ; this plane is also a gliding plane. The crystals are only feebly dichroitic: on  $\{001\}$  blue and pale blue. On  $\{001\}$  normal extinction; the plane of the optical axes is perpendicular to  $\{010\}$ ; the first bisectrix is almost perpendicular to  $\{001\}$ . The apparent axial angle is only small.

In thin layers, this salt has a red colour; it often appears in the final fractions of the crystallisation, but the crystalform and the composition are the same as here indicated.

In the case of copper nitrate, as well as in that of copper chloride<sup>1)</sup>, therefore, all three types of salts are possibly generated, in contrast to the case of copper *sulphate*, where only a *mono*- and a *tri*-dipyridyl derivative could be obtained.

§ 5. *Acetates*. From a solution of 1 mol. *copper acetate* with 1, 2 or 3 equivalents of dipyridyl a *mono-dipyridyl-copper acetate* of the composition:  $\left\{ \begin{array}{l} \text{Cu} \\ (\text{H}_2\text{O})_2 \end{array} \right\} (\text{C}_2\text{H}_3\text{O}_2)_2 + 3\text{H}_2\text{O}$  is obtained. Analysis yielded: 14.73%

<sup>1)</sup> F. M. JAEGER and J. A. VAN DIJK, these *Proceed.*, **37**, (1934) 395.

$\text{Cu}$ ; 6.49%  $N$  and 20.61%  $\text{H}_2\text{O}$ ; theoretically: 14.86%  $\text{Cu}$ , 6.55%  $N$  and 21.06%  $\text{H}_2\text{O}$ . The crystals have a rather dark blue colour with a reddish surface-hue; the prismatic needles are clearly dichroïtic: dark blue for vibrations parallel to their elongation, dark blue-violet for those perpendicular to this direction. They show an oblique extinction. The flat prisms are very badly built; in the vertical zone some angles were measured:  $b$  (broad and lustrous):  $m$  (narrow and not very lustrous) =  $29^\circ 19'$ ;  $m : p$  (like  $m$ , striated) =  $31^\circ 4'$ ;  $p : a$  (narrow, but well reflecting) =  $30^\circ 34'$ ;  $a : t$  (broader, well reflecting) =  $31^\circ 39'$ ;  $t : b' = 57^\circ 24'$ . Most probably the crystals are triclinic.

From the solution of copperacetate with 2 equivalents of dipyridyl, when slowly evaporated at  $15^\circ$ , an aggregation of blue crystals was obtained. As still the odour of the dipyridyl was perceptible, the crystals, after drying, were treated with ethylacetate. Analysis then yielded the following results: 11.68%  $\text{Cu}$ ; 18.84%  $\text{H}_2\text{O}$  and 48.0% dipyridyl, which corresponds to a *di*-dipyridyl-derivative, in which  $\frac{1}{3}$  molecule of the base is replaced by  $\frac{2}{3}$  mol. of water and containing 5  $\text{H}_2\text{O}$  as water of crystallisation:  $\left\{ \text{Cu} \begin{matrix} (\text{Dipyr})_{1.66} \\ (\text{H}_2\text{O})_{0.66} \end{matrix} \right\} (\text{C}_2\text{H}_3\text{O}_2)_2 + 5 \text{H}_2\text{O}$ . Of course, it also were possible, that here a mixture were present of 1 mol. of the salt formerly described:  $\left\{ \text{Cu} \begin{matrix} (\text{Dipyr}) \\ (\text{H}_2\text{O})_2 \end{matrix} \right\} (\text{C}_2\text{H}_3\text{O}_2)_2 + 3 \text{H}_2\text{O}$  and of 2 mol.  $\left\{ \text{Cu} (\text{Dipyr})_2 \right\} (\text{C}_2\text{H}_3\text{O}_2)_2 + 6 \text{H}_2\text{O}$ . Circumstances seem to be somewhat analogous as observed in the case of the salts of ironsulphate formerly investigated.

A pure salt with 2 mol. dipyridyl within its complex ion, never was obtained. A solution of copperacetate + 3 equivalents of dipyridyl gave a blue salt, yielding: 9.97%  $\text{Cu}$ ; 18.79%  $\text{H}_2\text{O}$  and 52.4% dipyridyl; as it still smells of dipyridyl, the crystals again were treated with ethylacetate: now they proved to contain: 8.51%  $N$ , 14.00%  $\text{Cu}$  and 12.53%  $\text{H}_2\text{O}$ . This composition corresponds to a salt of the formula:  $\left\{ \text{Cu} \begin{matrix} (\text{Dipyr})_{1.38} \\ (\text{H}_2\text{O})_{1.24} \end{matrix} \right\} (\text{C}_2\text{H}_3\text{O}_2)_2 + 2 \text{H}_2\text{O}$ . Evidently, the pure *di*-dipyridyl-salt cannot be obtained in this way; it always proves to be hydrolized to some extent.

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