Die Bildkurve φ^{20} hat demnach 2 *zehnfache* Punkte (U_1, U_2), 4 *vier-fache* Punkte S_k und 4 *Doppelpunkte* T_k.

Sie begegnet einer λ^{10} $(U_1^5 U_2^5 S_k^2 T_k)$ in 60 Punkten P. Die ϱ^3, welche φ berühren, bilden folglich eine *Fläche sechszigsten Grades*.

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

§ 1. Because indications are found in the literature of the subject concerning the existence in solution of complex cupric salts with a different number of *ammonia-, pyridine-,* and *chinoline*-molecules, — more especially in the case of *coppernitrate* and *coppersulphate*[1]), — we first tried to obtain the corresponding complex *dipyridylcoppersalts*. As a first object we tried *Coppermalonate*. This salt was prepared by the interaction of the theoretical quantity of malonic acid and freshly precipitated, thoroughly washed, colloidal cupric hydroxide. It crystallizes $(+ 3 H_2O)$ in the rhombic and pseudotetragonal form already described by HAUSHOFER[2]); the crystals are almost always parallel-growths in the shape of more or less perfect rhombic bipyramids and occasionally penetration-twins. The axial ratio of each single individuum and the optical properties were in complete agreement with those mentioned by HAUSHOFER: moreover, we observed the well-developed form $\{101\}$, which was not observed by the German author.

Aqueous solutions of this salt were mixed with 1, 2 and 3 equivalents of dipyridyl respectively in alcoholic solution and heated on the water-bath. Although the colour of the mixed solutions becomes more reddish-violet, the greater quantity of dipyridyl added is, — in all cases only a *mono*-dipyridyl-salt could be isolated, the excess of dipyridyl being deposited in the final motherliquors. The salt obtained crystallizes in parallelogram-shaped, flat, triclinic plates, which are often twins and which have a more or less dark blue colour: the differently coloured salts, however, all proved to have the same composition, their analysis yielding: 17,73 % Cu, 7,76 % N and 10,16 % H_2O. This corresponds to the formula: $\left\{ Cu \genfrac{}{}{0pt}{}{(Dipyr)}{(H_2O)_2} \right\} (C_3H_2O_4), \left\{ Cu \genfrac{}{}{0pt}{}{(Dipyr)}{(C_3H_2O_4)} \right\} + 2 H_2O$, or, — if the coordination-number is six, — perhaps to the formula: $\left\{ Cu \genfrac{}{}{0pt}{}{(Dipyr)}{(C_3H_2O_4)} \genfrac{}{}{0pt}{}{}{(H_2O)_2} \right\}$.

The water present is readily given off at 95° C.; the complex salt is

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[1]) M. AUMÉRAS and A. TAMISIER, Bull. de la Soc. Chim. de France, (4), **53**, (1933), 97, 102, 105, 111.

[2]) K. HAUSHOFER, Zeits. f. Kryst. **6**, (1882), 120.

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soluble in alcohol and the solution yields only a slight precipitate of silvermalonate, if silvernitrate is added to it; the precipitate, however, on standing gradually augments. It is, therefore, most likely, that the true composition is expressed by the latter formula and that, on contact with the aqueous solution, the salt is gradually changed into the salt of a composition as expressed by the first. This fact perhaps explains also the different colour of the preparations obtained. The triclinic crystals were measured by means of the bicircular goniometer[1]); they yielded the following angular values:

		Observed:	Calculated:
$b:c$	$=(010):(001)=^*$	69° 25′	—
$b:r$	$=(010):(\bar{1}01)=^*$	83 43	—
$b:m$	$=(010):(\bar{1}10)=^*$	54 16	—
$b:q$	$=(0\bar{1}0):(0\bar{1}1)=^*$	69 13	—
$m:q$	$=(1\bar{1}0):(0\bar{1}1)=^*$	66 45	—
$m:c$	$=(1\bar{1}0):(001)=$	90 52	90° 54′
$c:a$	$=(001):(100)=$	—	75 42

The forms observed are: $b=\{010\}$ predominant and very well reflecting; $m=\{1\bar{1}0\}$, narrow, yielding good reflections; $c=\{001\}$, very well developed and giving sharp images; $r=\{\bar{1}01\}$, small, giving somewhat dull reflections; $q=\{0\bar{1}1\}$, small, often absent. The crystals are tabular parallel to $\{010\}$ and often twins with the c-axis as twinning-axis; in goniometrical respect, the plane $\{1\bar{1}0\}$ is a plane of pseudo-symmetry. The crystals are perfectly cleavable parallel to $\{001\}$. The angular values show, with different individuals, rather appreciable oscillations.

The symmetry is triclinic-pinacoidal; the axial ratio, as deduced from the measurements, is:

$$a:b:c=1,019:1:0,7045;$$
$$A=110° 35\tfrac{1}{2}′ \quad ; \quad a=105° 20′$$
$$B=109 \quad 51 \quad ; \quad \beta=104 \quad 18$$
$$C=110 \quad 27\tfrac{1}{4} \quad ; \quad \gamma=105 \quad 9$$

The extinction on $\{010\}$ is oblique: about 15° with respect to the direction of the c-axis and in the twins mentioned above it is symmetrical with respect to the plane of pseudo-symmetry. The crystals are strongly dichroïtic: on $\{010\}$ for vibrations almost perpendicular to the plane $\{001\}$: bluish white; for those perpendicular to this direction: dark-blue.
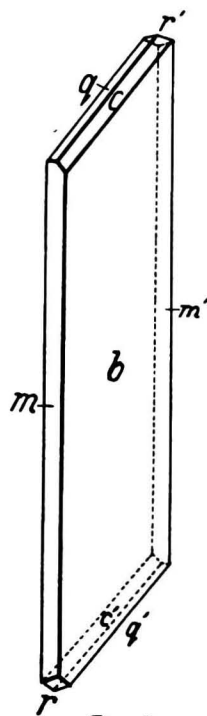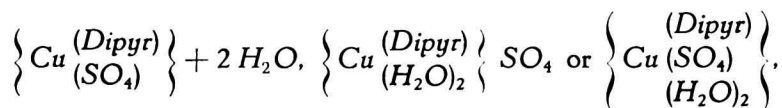

Fig. 1.

[1]) By Dr. TERPSTRA.

§ 2. As no other complex salt than this *mono*-dipyridyl-salt could be obtained, similar experiments were made, starting with *coppersulphate*: $CuSO_4 + 5H_2O$ and dipyridyl in alcoholic solution. Indeed, now we were able to obtain *two* different complex-salts: a pale blue *mono*-dipyridyl- and a dark blue *tri*-dipyridyl-salt of the compositions;

$$\left\{ Cu\,{(Dipyr) \atop (SO_4)} \right\} + 2\,H_2O, \quad \left\{ Cu\,{(Dipyr) \atop (H_2O)_2} \right\} SO_4 \ \text{or} \ \left\{ Cu\,(SO_4) {(Dipyr) \atop (H_2O)_2} \right\},$$

and $\{Cu\,(Dipyr)_3\}\,SO_4 + 7\,H_2O$ respectively.

If to a cold solution of 1 equivalent crystallized coppersulphate respectively 1, 2 or 3 equivalents of dipyridyl in a cold alcoholic solution are added, the blue colour of the solution turns to a deep violet and in the two first cases a pale blue, crystalline precipitate is formed, which is filtered-off, washed with water and dried. Its analysis yields the following data: 17,85 % Cu; 10,70 % H_2O; 7,13—7,8 % N. This corresponds to the *mono*-dipyridyl-salt: $\left\{ Cu\,{(Dip) \atop (SO_4)} \right\} + 2\,H_2O$. The pa'e blue salt is very sparingly soluble and has already been obtained by BLAU [1]; its water of crystallisation is partially given-off at 100° C., completely at about 120° C.

On the contrary, from the dark violet solution containing 3 equiva'ents of dipyridyl, on slow evaporation at room-temperature big dark-blue crystals of another salt are deposited. This is the *tri*-dipyridyl-salt: $\{Cu(Dip)_3\}\,SO_4 + 7H_2O$, as was proved by analysis: 8,44 % Cu; 61,8 % dipyridyl; 16,77 % H_2O [2]; calculated: 8,43 % Cu; 62,1 % dipyridyl and 16,72 % H_2O.

The complex salt crystallizes in mono-clinic, tabular crystals of rectangular habitus, which allow accurate measurements (Fig. 2). The symmetry is monoclinic-prismatic; the axial ratio is:

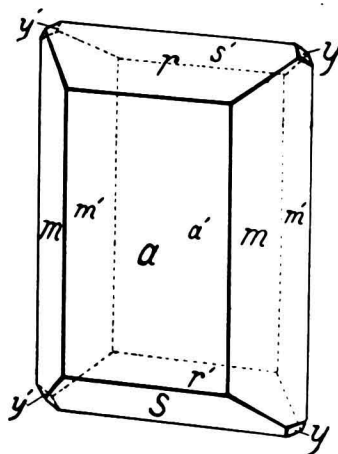$$a : b : c = 1,5466 : 1 : 0,9082 ;$$
$$\beta = 82° \ 8'.$$

Fig. 2.

Forms observed: $a = \{100\}$, broad, and very well reflecting; predominant, $m = \{110\}$,

$r = \{101\}$ and $s' = \{\bar{1}01\}$, all about equally well developed and yielding good reflections; $x = \{\bar{1}21\}$ and $y = \{011\}$, small, dull and only

[1] F. BLAU, Monatsh. f. Chem., **19**, (1898), 684.

[2] Ou heating, the crystals loose dipyridyl; the water-content, therefore, must be determined by keeping the powdered substance above concentrated sulphuric acid at roomtemperature.

approximately measurable; x often absent. The crystals are tabular parallel to $\{100\}$.

Angular Values:		Observed:		Calculated:	
$a:m$	$= (100):(110) =$*	$56°$	$52'$	—	
$a:r$	$= (100):(101) =$*	53	$49\frac{1}{2}$	—	
$a':s'$	$= (\bar{1}00):(\bar{1}01) =$*	65	33	—	
$m:m'$	$= (110):(\bar{1}10) =$	66	16	$66°$	$16'$
$r:s$	$= (101):(\bar{1}01) =$	60	$37\frac{1}{2}$	60	$37\frac{1}{2}$
$m':s'$	$= (\bar{1}10):(\bar{1}01) =$	76	59	76	$55\frac{1}{2}$
$m':x$	$= (\bar{1}10):(\bar{1}21) =$	ca.	$34°$	33	43
$x:y$	$= (\bar{1}21):(011) =$	ca.	$22°$	22	$32\frac{1}{2}$
$y:s$	$= (011):(10\bar{1}) =$	ca.	$47°$	46	49
$m:r$	$= (110):(101) =$	71	7	71	11

No distinct cleavability was observed.

The crystals are biaxial: on $\{100\}$ normal extinction. They are feebly dichroïtic: on $\{100\}$ for vibrations parallel to the c-axis: pale greenish-blue, for those perpendicular to that axis: blue.

§ 3. If the experiments are made in the same way, but this time starting from a *cold* solution of *copperchloride*, to which respectively 1, 2, or 3 equivalents of dipyridyl are added, *three* different products are obtained: a green *mono*-dipyridyl-salt, a blue *di*-dipyridyl- and a violet *tri*-dipyridyl-salt.

A. The green *mono*-dipyridyl-salt is very sparingly soluble[1]; it crystallizes in soft, green scales and, on analysis, yields: $21{,}87\%$ Cu; $24{,}35\%$ Cl; $9{,}54\%$ $N (= 53{,}2\%$ dipyridyl); theoretical: $21{,}87\%$ Cu; $24{,}4\%$ Cl: $9{,}64\%$ N.

Its composition, therefore, is: $\left\{ Cu \begin{matrix} (Dip) \\ Cl_2 \end{matrix} \right\}$; the salt is anhydrous and cannot be obtained in measurable crystals.

B. The blue salt crystallizes in moderately well developed crystals which, however, mostly form complicated aggregations, not allowing accurate measurements. By careful and slow evaporation of a saturated solution, we were able to obtain some small, tabular crystals, which in

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[1] On heating with water for a long time, the salt finally yields a *blue* solution, in which ionogen chlorine is present: evidently the complex ion is hydrolysed under these circumstances.

their aspect, remind us of those of the tri-dipyridyl-salt, but are clearly different from those (Fig. 3).

The crystals often have rounded edges; the angular values oscillate rather appreciably.

Rhombic — (bi)pyramidal.

$$a : b : c = 1,5805 : 1 : 0,9619$$

Forms observed: $a = \{100\}$, predominant, commonly yielding very sharp reflections; often $a = (100)$ is smooth, $a' = (\bar{1}00)$ vertically striated; $m = \{110\}$, well developed; its planes are vertically striated and yield broad and dull reflections; $o = \{111\}$, rather broad and giving sharp images; $q = \{011\}$, narrow and moderately reflecting; $b = \{010\}$, very small and gives dull reflections.

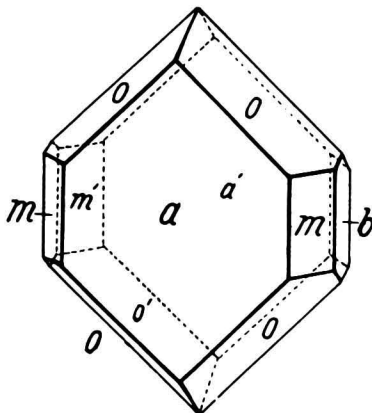*Fig. 3.*

Angular Values:		Observed:		Calculated:	
$o : o = (111) : (1\bar{1}1) =^*$		78°	49′	—	
$a : o = (100) : (111) =^*$		66	19	—	
$a : m = (100) : (110) =$		57°—57	38	57°	41′
$o : m = (111) : (110) =$		41	24	42	29
$b : o = (010) : (111) =$		50	36	50	$35\frac{1}{2}$
$b : m = (010) : (110) =$		32	22	32	$19\frac{1}{3}$
$o : q = (111) : (011) =$		23	41	23	41

No distinct cleavability was observed.

On $\{100\}$ normal extinction. The crystals are clearly dichroitic: on a for vibrations parallel to the c-axis: blue; for those perpendicular to them: pale greenish-blue.

The analysis yielded: $11,53\%$ Cu; $9,94\%$ $N (= 55,7\%$ dipyridyl); above concentrated sulphuric acid, the crystals loose $17,03\%$ H_2O, but, as on heating the salt at $100°$ and $130°$ C. it also looses dipyridyl under generation of the mono-dipyridyl-salt, — the total quantity of H_2O could not be determined by heating. For $\left\{ Cu \begin{matrix} (Dip)_2 \\ (H_2O)_2 \end{matrix} \right\} Cl_2 + 4 H_2O$ or $\{ Cu (Dip)_2 \} Cl_2 + 6 H_2O$, the calculated numbers are: $11,46\%$ Cu; $56,3\%$ dipyridyl and $19,43\%$ H_2O; so that there can be no doubt about the fact, that here the *di*-dipyridyl-salt is present.

C. The violet salt crystallizes in flat, hexagonally bordered, somewhat elongated plates. On analysis, the composition proved to be: $\{ Cu (Dip)_3 \} Cl_2 + 7 H_2O$; observed: $8,70\%$ Cu; $11,5\%$ $N (= 64,4\%$ dipyridyl); calculated: $8,72\%$ Cu and $64,3\%$ dipyridyl.

The crystals are rhombic-bipyramidal; the axial ratio is:

$$a : b : c = 2{,}0308 : 1 : 0{,}6131.$$

Forms observed: $a = \{100\}$, predominant and giving very sharp reflections; $m = \{110\}$, well developed; the faces are finely striated parallel to the c-axis, the reflections often broadened and somewhat dull; $b = \{010\}$, broader than m and like $\omega = \{111\}$, yielding very good images; $o = \{311\}$, smaller than ω, yielding somewhat dull reflections.

The habitus of the crystals is as reproduced in Fig. 4.

Angular Values:	Observed:	Calculated:
$a : m = (100):(110) =^*$	63° 47′	—
$\omega : \omega = (111):(\bar{1}11) =^*$	28 52	—
$m : b = (110):(010) =$	26 13	26° 13′
$a : o = (100):(311) =$	52 25	52 19½
$o : \omega = (311):(111) =$	23 4	23 14½
$a : \omega = (100):(111) =$	75 29	75 34
$\omega : \omega = (111):(\bar{1}11) =$	60 17	60 49
$b : \omega = (010):(111) =$	59 43	59 35½
$\omega : m = (111):(110) =$	55 48	55 39

No distinct cleavage was observed.

On a, m and b normal extinction; the crystals are, on $\{100\}$ only feebly dichroïtic.
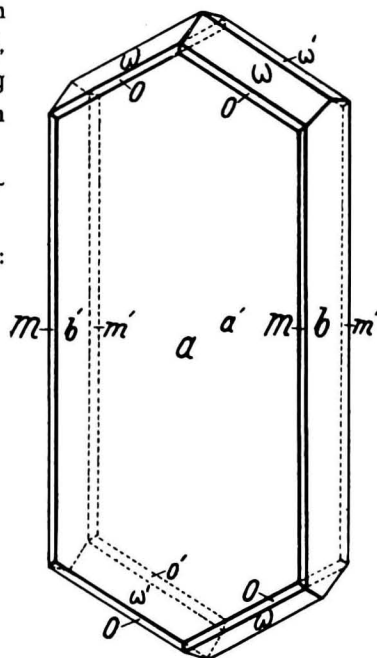

Fig. 4.

§ 4. These experiments clearly show, that the possibility of introducing 1, 2 or 3 molecules of dipyridyl into the complex cupric ion, is dependent on the nature of the anion: in *all* cases studied *mono*-dipyridyl-salts are formed; but in the case of the sulphate, moreover, a *tri*-dipyridyl, in that of the chloride *di*-, as well as *tri*-dipyridyl-salts can be formed besides the *mono*-derivatives. Such a dependency of the constitution of the complex ion on the anion was, to a lesser degree. recently also stated in the case of the ferrous salts [1]. From the paper of AUMÉRAS and TAMISIER (loco cit.) an analogous result seems to follow: in the case of copper*nitrate*, they stated the formation of only a *tetrammine*- or a *tetrapyridine*-complex, while in that of copper*sulphate*, as well a *di*- as a *tetrammine*-complex seems to be formed. By a further examination of these cases it must be decided, whether this fact really is connected with the more or less advanced hydrolytic decomposition, which these salts undergo in aqueous solutions at different temperatures.

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[1] F. M. JAEGER and J. A. VAN DIJK, these Proceed., **37**, (1934), 333.