Chemistry. — *On Complex Salts of Dipyridyl with Bivalent and Trivalent Cobaltum.* By F. M. JAEGER and J. A. VAN DIJK.

§ 1. Investigations analogous to those previously made[1]) concerning the complex salts of *dipyridyl* with bivalent metals like *iron, nickel, copper, zinc* and *cadmium*, finally were executed with bivalent *cobaltum*. In this case, however, greater difficulties were met with, because soon it became clear that undesired oxidation-phenomena caused the formation of accessory products derived from *tri*valent cobaltum, so that, according to the special circumstances during the preparation, different substances were obtained. Experience taught us that pure cobaltous salts of this type in most cases only could be obtained when working in a *reducing atmosphere*; as such an atmosphere of pure hydrogen was used, in which the crystallization of the solutions was performed by slow evaporation at room-temperature.

In this way from an aqueous solution of *cobaltous chloride*: $CoCl_2 + 6H_2O$, to which an excess of *dipyridyl* was added, big brown or dark orange-brown crystals were deposited, which proved to have the composition: $\{Co(Dipyr)_3\} Cl_2 + 6H_2O$, notwithstanding the fact that they are perfectly isomorphous with the corresponding *tridipyridyl* salts of the other series, containing $7H_2O$; repeated analyses, however, convinced us of this deviating water-content. As the salt considered proved to lose dipyridyl (1 mol.) at 100° C, the water-content had to be determined at temperatures below 100° C.; the analysis yielded: 8.29 % Co; 11.76 % N; 9.96 % Cl and 15.08 % H_2O, the theoretical numbers being: 8.35 % Co; 11.90 % N; 10.04 Cl and 15.30 % H_2O for a salt with $6H_2O$[2]).

The same compound can be obtained from a solution of *cobaltous chloride* with an excess of *dipyridyl*, through which a current of air was passed during several hours, in the form of pale orange-yellowish scales, which, in contrast to the bigger crystals, are mostly single while the large crystals are almost always twins, although occasionally also in the latter case single crystals could be obtained.

[1]) F. M. JAEGER and J. A. VAN DIJK, Proc. Royal Acad. Amsterdam, **37**, 10, 333, 395, 618, 753 (1934); **38**, 235, 972 (1935).

[2]) For a salt with $7H_2O$, the calculated values are: 8.14 % Co; 11.60 % N; 9.79 % Cl and 17.41 % H_2O. The isomorphism of the salt considered at once becomes evident on comparing its crystal form with that of the salt considered at once becomes evident on and *zinc*, all these containing $7H_2O$.

Monoclinic-prismatic.

$a : b : c = 0.6018 : 1 : 2.1353;$ $\beta = 73° 12\frac{1}{4}'.$

Forms observed: $c = \{001\}$ predominant, yielding ideal reflections; $m = \{110\}$, very well developed; $q = \{011\}$, mostly small, well reflecting; $r = \{\overline{1}01\}$, in most cases absent, with the twin crystals only developed at
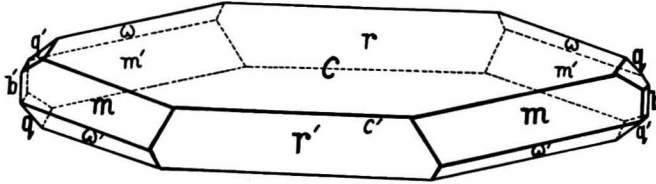

Fig.1. Tridipyridyl-Cobaltous-Chloride (+6H₂O).

one end of the a-axis, yielding moderate reflections and having, with the twin crystals, a fine horizontal line of division; with an angle of about 1°; $\omega = \{\overline{1}12\}$, very narrow, but well measurable. The thin orange-yellow scales showed, moreover, $t = \{013\}$, very narrow and only approximately measurable; $b = \{010\}$, small, but very lustrous. Moreover, sometimes the forms $\{012\}$ and $\{\overline{1}22\}$ were observed, both extremely narrow and hardly measurable. The habitus is tabular parallel to $\{001\}$; the twinning plane is $\{001\}$, with the a-axis as twinning axis.

Angular Values:	*Observed:*		*Calculated:*	
$c : m = (001) : (110) =^*$	75°	30′	—	
$m : m = (110) : (1\overline{1}0) =^*$	59	54	—	
$c : q = (001) : (011) =^*$	63	56	—	
$m : \omega = (110) : (11\overline{2}) =$	28	30	28°	$18\frac{3}{4}'$
$\omega : c = (\overline{1}12) : (001) =$	76	14	76	$11\frac{1}{4}$
$m : b = (110) : (010) =$	60	3	60	3
$q : q = (011) : (01\overline{1}) =$	52	8	52	8
$b : q = (010) : (011) =$	26	4	26	4
$c : t = (001) : (013) =$	34	0	34	$16\frac{1}{3}$
$m : q = (110) : (011) =$	56	0	56	3
$m : r = (\overline{1}10) : (\overline{1}01) =$	33	38	33	$50\frac{1}{2}$
$r : c = (\overline{1}01) : (001) =$	90	16	90	26
$m : m' = (110) : (110) =$	29	0	29	0
I II				

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

On $\{001\}$ diagonal extinction. In convergent polarized light the axial plane is found to be perpendicular to $\{010\}$; the first bissectrix is almost

perpendicular to {001}. The dispersion is horizontal and only moderate. The crystals are, on {001}, only feebly dichroitic.

§ 2. If to a solution of *cobaltous chloride* in water two equivalents of *dipyridyl* are added and the solution is evaporated in an atmosphere of hydrogen, the *tridipyridyl*-compound is deposited beside another, badly crystallizing product, which is the *monodipyridyl*-salt.

This *monodipyridyl*-salt afterwards was also obtained by adding 1 equiv. dipyridyl in alcoholic solution to an aqueous solution of $CoCl_2 . 6 H_2O$ and evaporating the solution in a vacuum-exsiccator over sulphuric acid in a reducing atmosphere (hydrogen) at room-temperature.

The salt is deposited as yellow-brown, badly crystallizing scales and small plates, which are very soluble. Analysis yielded: 15.87 % Co; 7.24 % N; 19.06 % Cl and 22.4 % H_2O; calculated for $\left\{ Co \dfrac{(Dipyr)}{Cl_2} \right\} +$ $5 H_2O$: 15.67 % Co; 7.45 % N; 18.86 % Cl and 23.95 % H_2O.

If, however, the same experiment is made with anhydrous $CoCl_2$ in an alcoholic solution, garnet-red crystals are deposited, which contain alcohol of crystallization and in a vacuum soon lose their alcohol of crystallization. When, in a reducing atmosphere, they are recrystallized from water, a garnet-red salt is deposited, which, according to the analysis, is the *dipyridyl*-salt of the constitution: $\left\{ Co \dfrac{(Dipyr)_2}{(H_2O)_2} \right\} Cl_2 + 4 H_2O$.

Their analysis yielded: 10.67 % Co; 10.18 % N; 12.91 % Cl and 16.7 % H_2O; calculated: 10.71 % Co; 10.18 % N; 12.89 % Cl and 16.40 % H_2O. But when the aqueous solution with 2 equivalents of *dipyridyl* is evaporated in the air, a dark brick-red salt, crystallizing in beautiful small plates is formed, which on analysis yielded: 11.43 % Co, 10.68 % N and 6.80 % H_2O.

Afterwards it was proved that this salt is a *cobaltic* salt, more particularly, the *di-dipyridyl-carbonato-cobaltic-chloride* of the composition: $\left\{ Co^{III} \dfrac{(Dipyr)_2}{(CO_3)} \right\} Cl + 2 H_2O$, for which the theoretical values are: 11.72 % Co; 11.15 % N and 7.17 % H_2O. Although no complete analysis could in this case be made, owing to lack of material as a consequence of some miscarried CARIUS-analyses, the full proof of the constitution of this kind of cobaltic salts will be given in the cases of the corresponding sulphate and nitrate. Finally it is worth while to remark here that in this oxidation process a small quantity of a violet salt, presumably of the *violeo*-salt: $\left\{ Co^{III} \dfrac{(Dipyr)_2}{Cl_2} \right\} Cl + 2 H_2O$ is simultaneously generated.

§ 3. When *cobaltous sulphate* in aqueous solution is treated with 2 equivalents of *dipyridyl* in a reducing atmosphere, two salts are deposited:

a monoclinic *tridipyridyl* salt of the composition: $\{Co(Dipyr)_3\}\,(SO_4) +$ $7\,H_2O$, isomorphous with the corresponding salts of *nickel, copper* and *cadmium*, and a triclinic *monodipyridyl* salt of the formula: $\left\{Co\begin{matrix}(Dipyr)\\(H_2O)_2\end{matrix}\right\}$ $(SO_4) + 4\,H_2O$, which is isomorphous with the analogously built *nickel-salt*.

The *tridipyridyl*-salt, on analysis, gave the following results: 7.84 % Co; 11.09 % N and 16.60 % H_2O; calculated: 7.86 % Co; 11.21 % N and 16.82 % H_2O. The *monodipyridyl*-salt was obtained in two differently coloured forms, the first one being pale pink and easily losing water of crystallization, the second having a more yellow or orange-reddish colour and not changing in the air. The two substances, on analysis, yield the same numbers: 6.73 % N; 14.29 % Co for *cobaltum* and *nitrogen*; but the water of crystallization given off oscillates between $4\,H_2O$ (16.90 %) H_2O with the orange salt, to 19.2 % with the pink salt.

Tridipyridyl-cobaltous-sulphate $(+ 7\,H_2O)$ crystallizes from its aqueous solutions in dark brown, lustrous and often rather irregularly developed crystals.

Monoclinic-prismatic [1]).

$$a : b : c = 1.5435 : 1 : 0.9527; \quad \beta = 81° 8\frac{1}{2}'.$$

Forms observed: $m = \{110\}$, $r = \{\bar{1}01\}$ and $s = \{101\}$, usually all about equally well developed; $a = \{100\}$, somewhat narrower; $q = \{011\}$, either
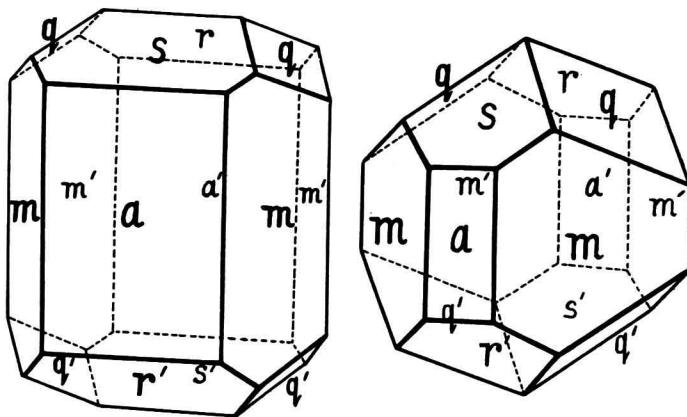

Fig. 2. Tridipyridyl-Cobaltous-Sulphate (+7H₂O)

as large as *s* and *r*, or much smaller. All these forms yield very good reflections; *q* sometimes only with two faces present, *a* often narrow.

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[1]) The monoclinic symmetry was also controlled by Dr. TERPSTRA by means of the bicircular goniometer, especially with the irregularly shaped specimens.

Angular Values: *Observed:*   *Calculated:*

$$a : r = (100) : (10\bar{1}) = * \ 64°\ 53' \qquad —$$
$$a : m = (100) : (110) = * \ 56\ \ \ 45 \qquad —$$
$$s : r = (101) : (\bar{1}01) = * \ 61\ \ \ \ 4 \qquad —$$
$$m : r = (110) : (10\bar{1}) = \ \ 76\ \ \ 42 \qquad 76°\ 32\tfrac{1}{2}'$$
$$m : m = (110) : (\bar{1}10) = \ \ 66\ \ \ 45 \qquad 66\ \ \ 30$$
$$m : q = (\bar{1}10) : (011) = \ \ 59\ \ \ 27 \qquad 59\ \ \ 12$$
$$a : s = (100) : (101) = \ \ 52\ \ \ \ 0 \qquad 52\ \ \ \ 3$$
$$m : s = (\bar{1}10) : (101) = \ \ 70\ \ \ \ 0 \qquad 70\ \ \ 18$$

No distinct cleavability was observed.

The plane of the optical axes is {010}; on {101} the crystals are strongly dichroitic: yellow and orange.

§ 4. The *monodipyridyl-diaquo-cobaltous-sulphate:* $\left\{ Co\ \dfrac{(Dipyr)}{(H_2O)_2} \right\}$ $(SO_4) + 4H_2O$, which is obtained as a by-product in the preparation of the *tridipyridyl* salt in a reducing atmosphere, crystallizes in pale yellow or darker yellow-orange long needles (Fig. 3).

Triclinic-pinacoidal.

$$a : b : c = 1{,}8383 : 1 : 1{,}1894;$$
$$A = \ 76°\ 57' \ ; \ \alpha = 78°\ 24'.$$
$$B = 128\ \ \ 18 \ \ \ ; \ \beta = 127\ \ \ 45.$$
$$C = \ \ 83\ \ \ 31 \ \ \ ; \ \gamma = \ \ 92\ \ \ 28\tfrac{1}{2}.$$

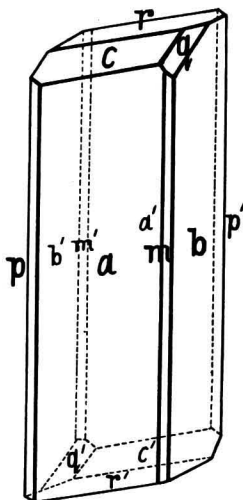*Forms observed:* $a = \{100\}$ and $b = \{010\}$, about equally broad

Fig. 3. Monodipyridyl-diaquo-Cobaltous-Sulphate.
(+4H₂O).

and very lustrous; $c = \{001\}$ and $r = \{101\}$, well developed, about

equally broad and yielding very sharp reflections; $m = \{110\}$ and $p = \{1\bar{1}0\}$, usually narrow and only with two faces present; m reflects better than p; $q = \{011\}$, small, but very well measurable. The crystals are long isometrically developed prisms parallel to the c-axis.
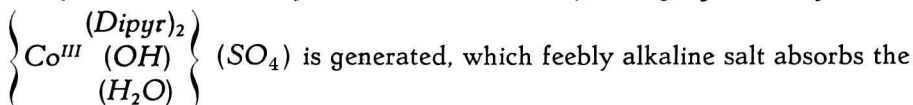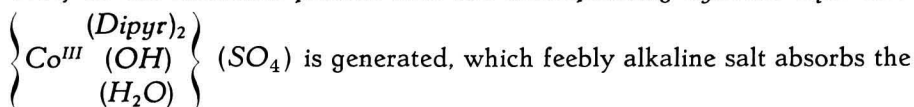
Angular Values:	Observed:		Calculated:	
$a : b = (100) : (010) =$*	96°	29'	—	
$b : c = (010) : (001) =$*	103	3	—	
$a : c = (100) : (001) =$*	51	42	—	
$c : r = (001) : (101) =$*	39	22	—	
$a : m = (100) : (110) =$*	60	33	—	
$r : a = (101) : (100) =$	88	56	88°	56'
$b : m = (010) : (110) =$	35	56	35	56
$a : p = (100) : (1\bar{1}0) =$	54	53	54	$43\frac{1}{2}$
$c : q = (001) : (011) =$	47	48	47	31
$b : p = (0\bar{1}0) : (1\bar{1}0) =$	28	38	28	$47\frac{1}{2}$
$b : q = (010) : (011) =$	55	15	55	32
$b : r = (010) : (101) =$	78	27	78	$21\frac{1}{2}$

No distinct cleavability was observed.

On $\{010\}$ the crystals are only feebly dichroitic, on $\{100\}$ much more strongly: yellow and orange. The principal optical sections are, on $\{100\}$ and on $\{010\}$, oblique to the direction of the c-axis, inclining towards m under angles of about 46°—48°.

The more yellowish-orange tinged crystals hitherto could not be obtained in a measurable form; so that it still remains questionable, whether they are identical with those of the other preparation, or not.

§ 5. From an aqueous solution of cobaltous sulphate + 2 equivalents of *dipyridyl*, which for a long time was exposed to the air, chiefly garnet-red crystals of a *dipyridyl-cobaltic*-salt are obtained, which on analysis proved to be the *di-dipyridyl-carbonato-cobaltic-sulphate* of the composition: $\left\{ Co^{III} \dfrac{(Dipyr)_2}{(CO_3)} \right\}_2 (SO_4) + 9 H_2O$. Analysis gave: 10.43 % Co; 9.94 % N; 8.61 % (SO_4) and 13.7 % H_2O; calculated: 10.52 % Co; 10.0 % N; 8.77 % (SO_4) and 14.47 % H_2O. On treating the salt with concentrated HCl, carbondioxide is set free; the evaporated solution then yields the corresponding *violeo*-salt, which on dissolving gives an orange-red solution, after initially passing through a violet-red colour. Most probably in the oxidation process first the corresponding *hydroxo-aquo*-salt: $\left\{ Co^{III} \begin{matrix} (Dipyr)_2 \\ (OH) \\ (H_2O) \end{matrix} \right\} (SO_4)$ is generated, which feebly alkaline salt absorbs the

carbondioxide from the air so as to form the carbonato-salt. Similar reactions occur in the case of the nitrate and of the halogenides; they clearly demonstrate the great tendency of the cobaltous ion to pass into the trivalent state under these circumstances.

The same carbonato-salt also is produced, if solutions of cobaltous sulphate with 1 or 3 equivalents of dipyridyl are oxidized by the air; in the latter case the solution, moreover, proved to contain free dipyridyl. There can, therefore, be no reasonable doubt about the correctness of the supposed reaction, more particularly since the transformation of such hydroxo-aquo-cobaltic salts into the corresponding carbonato-salts by the action of carbondioxide has already been previously stated by WERNER [1]).

§ 6. If to an aqueous solution of *cobaltous nitrate* 3 equivalents of *dipyridyl* are added and then it is slowly evaporated in a reducing atmosphere, thin flat needles of a yellowish-brown colour are deposited, which ordinarily exhibit a number of badly developed faces and which show considerable oscillations of their angular values. Although the corresponding angles on an anerage differ $1°—1°.5$ from those of the *tridipyridyl-coppersalt* ($+ 6 H_2O$), the crystals doubtlessly are isomorphous with those of the latter salt. Analysis yielded: 7.88 % Co; 14.74 % N; 16.23 % (NO_3); and 14.16 % H_2O; theoretically, for $\{Co(Dipyr)_3\}$ $(NO_3)_2 + 6 H_2O$: 7.76 % Co; 14.76 % N; 16.33 % (NO_3) and 14.23 % H_2O.

The crystals are *monoclinic-prismatic*; from the angular values chosen, their axial ratio is calculated to be:

$$a : b : c = 1.7568 : 1 : 1.7125; \quad \beta = 86° \ 20\frac{1}{2}'.$$

Forms observed: $c = \{001\}$ predominant and very lustrous; $a = \{100\}$, much narrower than c, but yielding good reflections; $\omega = \{111\}$, well
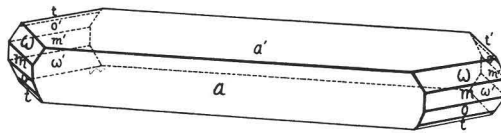

Fig. 4. Tridipyridyl-Cobaltous-Nitrate (+6H₂0).

developed; $o = \{1\bar{1}1\}$, mostly narrower than ω, like $m = \{110\}$ and yielding oscillating angular values; sometimes very narrow and only approximately measurable, $s = \{661\}$ and $t = \{11\bar{2}\}$. The habitus is tabular parallel to $\{001\}$, with a strong elongation in the direction of the b-axis. (Fig. 4).

Angular Values:	*Observed:*	*Calculated:*
$a : c = (100) : (001) =^* 86° \ 20\frac{1}{2}'$		—
$a : \omega = (100) : (111) =^* 62 \quad 10 \ (61° 54'—62° 24')$		—
$c : \omega = (001) : (111) =^* 61 \quad 29 \ (60° 52 \ —61° 42')$		—

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[1]) A. WERNER, Ann. d. Chem., **386**, 101 (1912).

Angular Values: *Observed:*   *Calculated:*

$c : o = (00\bar{1}) : (11\bar{1}) =$	63° 10′—64° 20′	64° 30′
$\omega : s = (111) : (661) =$	21°—22°	21 52½
$\omega : m = (111) : (110) =$	27°—28° 40′	26 43
$s : m = (661) : (110) =$	ca. 6°	5 26½
$m : t = (110) : (11\bar{2}) =$	ca. 26°—27°	27 18
$t : o = (11\bar{2}) : (11\bar{1}) =$	ca. 16°—17°	19 5
$t : c = (11\bar{2}) : (001) =$	ca. 47°	45 25
$a' : o = (\bar{1}00) : (\bar{1}11) =$	65° 20′—66° 8′	65 19

Cleavable parallel {001}; the crystals are only very feebly dichroitic. On {001} normal extinction; the plane of the optical axes for most colours is perpendicular at {010}, for the red rays, however, parallel to it. Rather small optical angle; the first bissectrix is almost perpendicular to {001}.

§ 7. When an alcoholic solution of 1 equivalent dipyridyl is added to an aqueous solution of *cobaltous nitrate*, the latter gets an orange-red colour. If slowly evaporated in a hydrogen-atmosphere in a vacuum-exsiccator over H_2SO_4, the finally syrupy liquor deposits pink-orange, not measurable crystals of the highly soluble *monodipyridyl-cobaltous-nitrate* of the composition $\left\{ Co \begin{matrix} (Dipyr) \\ (NO_3)_2 \end{matrix} \right\} + 3 H_2O$ or the *diaquo*-salt: $\left\{ Co \begin{matrix} (Dipyr) \\ (H_2O)_2 \end{matrix} \right\} (NO_3)_2 + 1 H_2O$, as is proved by its analysis: 14.85 % Co; 14.05 % N; 30.79 % (NO_3) and 13.56 % H_2O; calculated: 14.99 % Co; 14.25 % N; 31.54 % (NO_3) and 13.75 % H_2O.

§ 8. When to the solution of *cobaltous nitrate* an alcoholic solution of 2 equivalents of dipyridyl is added and it is subsequently exposed to the air, in all cases a garnet-red salt, crystallizing in thin needles or sometimes in thicker parallelogram-shaped crystals, is formed. Analysis showed that this salt is the *di-dipyridyl-carbonato-cobaltic-nitrate* of the composition: $\left\{ Co^{III} \begin{matrix} (Dipyr)_2 \\ (CO_3) \end{matrix} \right\} (NO_3) + 5 H_2O$, as follows from the values obtained: 10.21 % Co; 12.12 % N; 10.75 % NO_3 and 14.93 % H_2O; calculated: 10.11 % Co; 12.01 % N; 10.63 % (NO_3) and 15.44 % H_2O. The salt shows with concentrated hydrochloric acid a liberation of CO_2; the colour of the solution first turns violet and later orange-red.

The crystals usually only a show rudimentary development of their terminal faces. Some specimens were better built and well measurable.

Monoclinic-prismatic.

$a : b : c = 0.9033 : 1 : 0.6834; \quad \beta = 77° 22\frac{1}{2}′.$

Forms observed: $b = \{010\}$, mostly predominant or equally broad as $q = \{011\}$, both yielding excellent reflections; $\omega = \{\bar{1}11\}$, well developed,

giving good images, often only with two faces; the form $a = \{100\}$ is often absent, yields very bad reflections and is only approximately measurable.
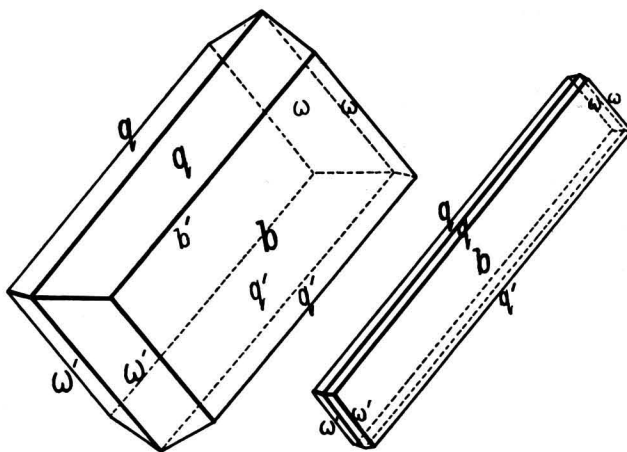

Fig. 5. Di-dipyridyl-carbonato-Cobaltic-Nitrate (+5 H₂O).

The habitus is thin, tabular, parallel to $\{010\}$ or more isometrically developed in the bigger crystals, which often show q, ω and b in almost equal development (Fig. 5).

Angular Values:		Observed:		Calculated:	
$b : q$	$= (010) : (011) =*$	56°	18′	—	
$b : \omega$	$= (010) : (\bar{1}11) =*$	59	6	—	
$q : \omega$	$= (0\bar{1}1) : (\bar{1}11) =*$	75	32	—	
$q : q$	$= (011) : (0\bar{1}1) =$	67	24	67°	24′
$\omega : \omega$	$= (\bar{1}\bar{1}1) : (\bar{1}11) =$	61	44	61	48
$q : \omega$	$= (011) : (\bar{1}11) =$	34	59	34	$57\frac{1}{3}$

No distinct cleavability was found; perhaps there is an imperfect one parallel to $\{010\}$. One of the optical directions on $\{010\}$ includes an angle of about 50° with the edge $q : b$ and points towards a'. At the border of the field one of the branches of a dark hyperbola is visible in convergent light. The crystals are on $\{010\}$ only unappreciably dichroitic.

§ 9. *Praseo- and Violeo-Cobaltic-Salts.*

6.24 Grammes of dipyridyl were added to an aqueous solution of 4.76 grammes of $CoCl_2 + 6 H_2O$; then 40 cm³ of a 10 %-solution of hydrogenperoxide were slowly and in small quantities gradually added under continuous stirring of the mixture. The solution turns dark brown; when the reaction is completed, the solution is heated on the water-bath so as to decompose the hydrogenperoxide in excess and then 75 cm³ of strong hydrochloric acid are added. The dark green solution is evaporated on the

water-bath, till a thick, green and sticky residue remains, which is further dried in a vacuum-exsiccator over lime. The dry mass obtained now was repeatedly extracted with absolute alcohol to remove the hydrochloric acid; the green product proved still to contain inclusions of a violet colour. On extracting this mixture with *boiling* absolute alcohol, the violet product proved to be readily soluble in it, whilst the green one was not. From the hot alcoholic solution, on cooling, very beautiful, lustrous small tables or thin scales of a dark violet colour were deposited, which, according to their analysis, represented those of the pure *violeo*-salt: $\left\{ Co^{III} \dfrac{(Dipyr)_2}{Cl_2} \right\} Cl +$ $2H_2O$; found: 11.46 % Co; 10.79 % N; 20.68 % Cl and 6.99 % H_2O; calculated: 11.48 % Co; 10.96 % N; 20.71 % Cl and 7.01 % H_2O. The salt dissolves in water with a violet colour which, however, soon changes into orange-red.

The green product proved to be an impure *praseo*-salt; notwithstanding many tentatives, it could not be obtained in the pure form, but its analysis finally yielded the incorrect values: 12.71 % Co; 20.68 % Cl; 9.30 % N and 9.30 % H_2O. There can, however, be no doubt that the *praseo*-salt really is present in this preparation in a predominant quantity.

Tentatives were made to obtain a *dipyridyl-diethylenediamine*-salt by boiling an aqueous solution of the *praseo-diethylenediamine*-salt with the calculated amount of *dipyridyl* in alcohol at a reflux-cooler under exclusion of the carbondioxide of the air. The products obtained were, however, *tri-dipyridyl-cobaltous-chloride,* which was deposited in brilliant yellow tables, and *tri-ethylenediamine-cobaltic-chloride*; so that evidently a partial reduction of the cobaltic ion to the cobaltous state has occurred during this reaction.

§ 10. *Tridipyridyl-Cobaltic-Sulphate and -Chloride.*

By electrolysis of an acid solution of *cobaltous sulphate* under well-known conditions, a green product can, by anodic oxidation, be obtained, which chiefly consists of a mixture of an excess of *cobaltic sulphate* and some unchanged cobaltous salt + sulphuric acid. The green mass was rapidly freed from the excess of the acid and of water and then immediately treated with a solution of more than 3 equivalents of dipyridyl. Besides some *tridipyridyl-cobaltous-sulphate*, a yellowish-brown substance, crystallizing in small, lustrous scales, was obtained, which undoubtedly is the *tridipyridyl-cobaltic-sulphate* desired. Its analysis yielded: 7.0 % Co; 10.0 % N; 25.11 % (SO_4) and 12.11 % H_2O, which corresponds to about $\{Co^{III}(Dipyr)_3\}_2 (SO_4)_3 + 5H_2O$ with an excess of about 5 % sulphuric acid.

From the solution of this salt (SO_4) was precipitated by means of the calculated quantity of *bariumchloride*; the filtered solution was evaporated upon the water-bath and the dark brown-red, syrupy solution, finally remaining, left for crystallization in a vacuum-exsiccator over sulphuric

acid. Beautiful, very lustrous prismatic crystals were deposited from it, which proved to be the *tridipyridyl-cobaltic-chloride*: $\{Co^{III}(Dipyr)_3\}Cl_3 + 3\,H_2O$. The analysis [1]) yielded: 8.38 % Co; 12.06 % N; 15.09 % Cl and 7.74 % H_2O; calculated: 8.57 % Co; 12.22 % N; 15.47 % Cl and 8.04 % H_2O.

The salt is *rhombic-bipyramidal* and isomorphous with the corresponding *rhodium*-salt [2]). As only the forms: $a = \{100\}$, $m = \{110\}$ and $c = \{001\}$
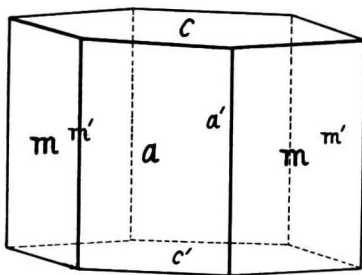

Fig. 6. Tridipyridyl-Cobaltic-Chloride (+3 H₂O).

occur and no terminal faces were ever observed, only the axial ratio $a : b = 0.858 : 1$ could be determined by direct measurement.

Angular Values:

$$a : m = (100) : (110) =^* \quad 40° \ 38' \qquad —$$
$$a : c = (100) : (001) =^* \quad 90 \quad 0 \qquad\ —$$
$$m : m = (110) : (\bar{1}10) = \quad 98 \quad 44 \qquad 98° \ 44'$$

The crystals are well cleavable parallel to $\{100\}$; the plane shows a fine vertical striation.

Normal optical extinction; the plane of the optical axes is $\{010\}$, with the *a*-axis as first bissectrix and a very small apparent angle. Strongly dichroitic: on $\{100\}$ for vibrations parallel to the *c*-axis yellow, for those parallel to the *b*-axis blood-red.

§ 11. Finally once more attention may be drawn to the fact that, as already mentioned, the *same* metal can in aqueous solutions form different types of complex ions, *depending on the special nature of the anion*: thus e.g. *nickel* forms complex *chlorides* and *sulphates* only with 3 or 1 dipyridyl, but *nitrates* with 3, 2 and 1 molecules of the base, etc. From the following table these particularities may easily be seen; also the differences in behaviour in this respect of *different* metals in connection with the *same* anion:

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[1]) Chlorine was determined by a CARIUS-analysis, cobaltum as $CoSO_4$ and the water-content in vacuo over P_4O_{10}; nitrogen by micro-analysis according to DUMAS.

[2]) F. M. JAEGER and J. A. VAN DIJK, Proc. Royal Acad. Amsterdam, **37**, 286 (1934).

	Synopsis of the Salt-Types observed.		
Bivalent Metals:	**Chlorides:**	**Nitrates:**	**Sulphates:**
Iron	3 —— 1? (7) 6		3* —— 1* (5) (3)
Nickel	3 —— 1 (7) (2)	3 2 1 5) (3) (3)	3 —— 1 (7) (4)
Cobaltum	3 —— 1 (6) (5)	3 — 1 (6) (3)	3 —— 1 (7) (6)
Zinc	3 —— 1(a) (7)	3 —— 1 (6) (3)	3 —— 1 (7) (2)
Copper	3 2 1(a) (7) (6)	3 2 1 (6) (1) (3)	3 —— 1 (7) (2)
Cadmium	— 2 1(a) (1)	3 2 1 (7) (0.5) (2)	3* —— 1 (3) (4)
Trivalent Metals:			
Cobaltum	3 2 — (3) (2)	3 2 — 5)	3 2 — (5) (4.5)
Rhodium	3 2* 1* (3)		

Legenda:
Copper malonate: only 1 (2).
Copper acetate: *2 —— 1.
           (5)   (5)
a means: *anhydrous* salt; * means *hydrolizing* ions.
The small numbers between ( ) mean: the number of molecules of water of crystallization (or in the complex ion) of the salt considered.

thus e.g. *nickel, copper* and *cadmium* as *nitrates* will yield complex ions with 3, 2 and 1 molecules dipyridyl, whilst *zinc* and *cobaltum* only form complex salts with 3 and 1 dipyridyl. The tendency to form complexes of this kind is strongest with *copper*; but even here the *malonate* can yield a complex ion with only 1 molecule, the *acetate* with 1, perhaps with 2 molecules of the base, although in the latter case the second molecule is rather loosely bound and easily substituted by water. In general, the complex ions of the trivalent metals are much less subjected to the hydrolyzing agency of the solvent and, in consequence, appreciably more stable.

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