

TABELLE IV. Die mittlere Lichtkurve.

Phase	ν	Phase	ν	Phase	ν	Phase	ν
– 80 ^d	9.67 ^m	– 10 ^d	12.70 ^m	+ 60 ^d	9.88 ^m	+ 130 ^d	7.95 ^m
– 70	10.21	0	12.77	+ 70	9.14	+ 140	8.42
– 60	10.74	+ 10	12.68	+ 80	8.40	+ 150	8.92
– 50	11.25	+ 20	12.42	+ 90	7.76	+ 160	9.45
– 40	11.72	+ 30	11.95	+100	7.46	+ 170	9.98
– 30	12.15	+ 40	11.30	+110	7.37		
– 20	12.47	+ 50	10.62	+120	7.54		

Die Streuung ist wieder grösser beim Maximum und grösser im aufsteigenden Aste. Das Verhältnis der Streuungen 0.292 und 0.177 ist 1.65, das Verhältnis der durchschnittlichen Geschwindigkeiten des Lichtwechsels bei Auf- und Abstieg ist 1.22.

Utrecht, Februar 1935.

Chemistry. — *On Complex Salts of α - α' -Dipyridyl with Zinc and Cadmium.* II. By F. M. JAEGER and J. A. VAN DIJK.

(Communicated at the meeting of February 23, 1935.)

§ 1. In continuation of our previous paper on this subject¹⁾, we have studied the complex salts of some other *zinc*- and *cadmium*-salts with *α - α' -dipyridyl*, for the purpose of a comparison of the influence of the anions of the salts used on the structural type of the complex ion produced.

1. *Zincsalts*. On preparing the complex salts of the base with *zinc-nitrate* in the usual way, we only obtained *two* salts: a *mono*- and a *tridipyridyl*-salt. From a solution of one molecule of both constituents, on slow evaporation colourless, flat crystals are obtained, having the constitution: $\left\{ \text{Zn} \begin{matrix} (\text{Dipy}^r) \\ (\text{H}_2\text{O})_2 \end{matrix} \right\} (\text{NO}_3)_2 + 1 \text{H}_2\text{O}$. Analysis yielded: 16,11% Zn; 13,93% N; and 13,33% H_2O ; theoretically: 16,36% Zn; 14,02% N and 13,53% H_2O .

Monodipyridyl-diaquo-Zinc-nitrate crystallises from its motherliquors under these circumstances in the form of thin, hexagonally-shaped, transparent plates.

¹⁾ These Proceedings, 37, (1934), 753.

The salt is *monoclinic-prismatic* with:

$$a : b : c = 1,5408 : 1 : 2,4102;$$

$$\beta = 71^\circ 52'.$$

Forms observed: $c = \{001\}$, predominant, lustrous, but often yielding multiple reflections; $a = \{100\}$, mostly well reflecting, in some cases

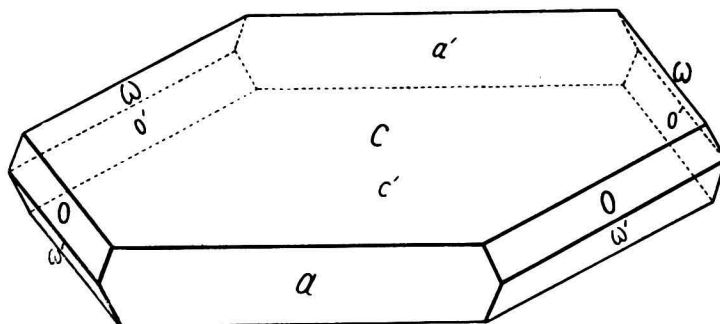


Fig. 1. Monodipyridyl-Zinc-nitrate.

dull and curved; $o = \{111\}$, lustrous and broader than $\omega = \{\bar{1}\bar{1}\bar{1}\}$, which yields somewhat duller reflections. The crystals are often badly built: the corresponding angular values sometimes oscillate between limits of 1° or 2° . The habitus is tabular parallel to $\{001\}$, often with an elongation in the direction of the b -axis. (Fig. 1).

Angular Values:	Observed:	Calculated:
$a : c = (100) : (001) =^*$	$71^\circ 52'$	—
$a : o = (100) : (111) =^*$	$52 \quad 54$	—
$c : o = (001) : (111) =^*$	$61 \quad 26$	—
$c : \omega = (001) : (\bar{1}\bar{1}\bar{1}) =$	$79 \quad 35$	$79^\circ 21\frac{1}{4}'$
$o : \omega = (111) : (\bar{1}\bar{1}\bar{1}) =$	$61 \quad 53$	$62 \quad 2$
$a : \omega = (\bar{1}00) : (\bar{1}\bar{1}\bar{1}) =$	$64 \quad 34$	$65 \quad 4$
$o : \omega = (111) : (\bar{1}\bar{1}\bar{1}) =$	$39 \quad 40$	$39 \quad 13$
$\omega : \omega = (\bar{1}\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	$78 \quad 39$	$78 \quad 54$

No distinct cleavability was observed.

The plane of the optical axes is $\{010\}$; on $\{001\}$ one of the axes emerges at the border of the field.

§ 2. From solutions containing one equivalent of *zinc-nitrate* with two or three equivalents of *dipyridyl*, only a *tridipyridyl-salt* of the composition: $\{Zn(Dipyr)_3\}(NO_3)_2 + 6H_2O$ could be isolated, which proved to be completely analogous to the corresponding *cadmium-salt*

formerly described, although the latter probably contains $7H_2O$. Exactly as in the latter case, the crystals of the *zinc*-salt are sticky, flat, hexagonally-shaped tables, which have curved faces and are very badly built: the angular values show most appreciable oscillations amounting to $1^\circ, 2^\circ$ or more; the faces of $\{101\}$ and $\{011\}$ are in most cases finely striated. Evidently an isomorphism between the *zinc*- and the *cadmium*-salt is present; sometimes the crystals are twins according to $\{110\}$. Only approximate measurements are possible.

Rhombic-bipyramidal.

$$a : b : c = 0,936 : 1 : 0,889.$$

Forms observed: $m = \{110\}$, predominant, lustrous and yielding good images; $r = \{101\}$ and $q = \{011\}$ very small, dull and curved; sometimes there is an indication of the presence of $b = \{010\}$.

Elongated thin tables parallel to $\{110\}$; for their aspect, see Fig. 4 on page 757 of these Proceedings.

Angular Values:	Observed:	Limits:	Calculated:
$m : m = (110) : (\bar{1}\bar{1}0) =^*$	$86^\circ 12'$	$(85^\circ - 87^\circ)$	—
$m : r = (110) : (101) =^*$	$59 \quad 48$	$(55^\circ - 59\frac{1}{2}^\circ)$	—
$m : q = (110) : (011) =$	$62 \quad 25$	$(61^\circ - 63^\circ)$	$62^\circ 59\frac{1}{2}'$
$r : \omega = (101) : (112) =$	ca. 30°	—	$28 \quad 36$
$\omega : q = (112) : (011) =$	ca. 29°	—	$28 \quad 36$

No distinct cleavability was observed.

The crystals are in most cases flattened parallel to two faces of $\{110\}$. Twins parallel to $\{110\}$.

The plane of the optical axes is vertical, most probably parallel to $\{010\}$, with the *a*-axis as first bissectrix. Strong rhombic dispersion, with $p > v$ round the first bissectrix.

Analysis yielded: 8,80 % *Zn*; 14,62 % *N*; 16,33 % NO_3 and 13,78 % H_2O ; theoretically: 8,54 % *Zn*; 14,63 % *N*; 16,19 % NO_3 and 14,11 % H_2O .

§ 3. *Cadmiumsalts.* From a solution of equal molecules of *cadmium-sulphate* ($+ \frac{2}{3} H_2O$) and dipyridyl immediately a badly soluble, white precipitate is formed, which after filtering off, washing with a little alcohol and drying, proved to be the *monodipyridyl*-salt of the composition: $\left\{ Cd \begin{matrix} (Dipyr) \\ (H_2O)_2 \end{matrix} \right\} (SO_4) + 2 H_2O$. Analysis: 25,26 % *Cd*; 6,44 % *N* and 16,53 % H_2O ; calculated: 25,74 % *Cd*; 6,41 % *N* and 16,50 % H_2O . From the mother-liquor, which by traces of iron is coloured pale pink,

on slow evaporation at room temperature, small, beautifully crystallised individuals are deposited; on analysis they prove to have the same composition.

Monoclinic-prismatic.

$$a : b : c = 1,0292 : 1 : 1,7157;$$

$$\beta = 84^\circ 19'.$$

Forms observed: $c = \{001\}$, very lustrous and predominant; $m = \{110\}$, large and well developed yielding sharp reflections; $b = \{010\}$, smaller,

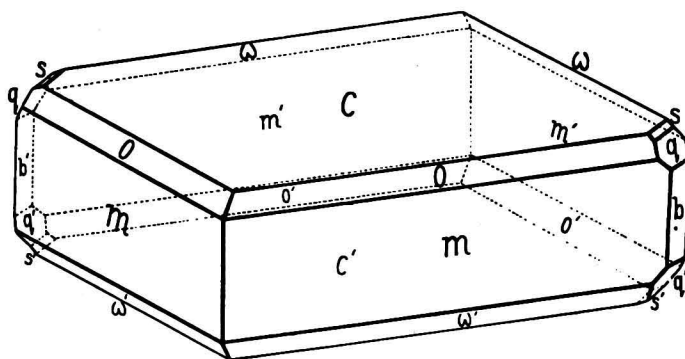


Fig. 2. Monodipyridyl-diaquo-Cadmium-sulphate.

but very brilliant; $q = \{011\}$, $s = \{012\}$, both small, q larger than s , but yielding good reflections; $o = \{112\}$ and $\omega = \{1\bar{1}2\}$, very narrow and somewhat dull. The habitus is tabular parallel to $\{001\}$ (Fig. 2).

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$m : m = (110) : (1\bar{1}0) =^*$	$91^\circ 22'$	—
$m : c = (110) : (001) =$	87 30	—
$b : q = (010) : (011) =$	30 25	—
$m : b = (110) : (010) =$	44 19	$44^\circ 19'$
$q : s = (011) : (012) =$	19 10	$19 1\frac{1}{2}$
$s : c = (012) : (001) =$	40 25	$40 33\frac{1}{2}$
$c : o = (001) : (112) =$	46 45	$46 53\frac{1}{2}$
$o : m = (112) : (110) =$	40 45	$40 36\frac{1}{2}$
$m : \omega = (110) : (1\bar{1}2) =$	40 59	$40 55\frac{1}{2}$
$\omega : c = (1\bar{1}2) : (00\bar{1}) =$	51 31	$51 34\frac{1}{2}$
$c : q = (001) : (011) =$	59 35	59 35

No distinct cleavability was observed.

On $\{001\}$ one of the directions of the optical extinction is normally orientated and perpendicular to the direction of the a -axis. In convergent light one observes a black hyperbola on c in an excentrical position.

Although fairly soluble, the salt has a smaller solubility than the corresponding *tridipyridyl*-salt.

§ 4. From a solution of one molecule of *cadmiumsulphate* with two, as well as with three molecules of dipyridyl, first a small quantity of the white precipitate already mentioned is precipitated; then, after evaporating in vacuo and slow evaporation of the motherliquor, big, lustrous crystals are deposited, which, in the two cases prove to have the same crystalforms.

Analysis yielded, in the case of 2 equivalents of the base being added, the following data: 17,87% Cd ; 10,21% N ; 15,26% SO_4 .

In the case of 3 equivalents of the base being added to the solution, the quantity of the precipitate is negligible; the mother-liquor evaporated in vacuo, yields big, colourless crystals, which, on analysis, yield: 16,94% Cd ; 10,43% N ; 14,48% SO_4 .

From this it follows, that principally the salt is a *tridipyridyl* — compound of the composition: $\{Cd(Dipyr)_3\}(SO_4) + 3H_2O$; but in the first case, there are about 2,3, in the second about 2,5 equivalents of the base on 1 equivalent of *cadmium*. Evidently here a part of the base in the complex ion is substituted by water, the total H_2O — content of the salt being in both cases 3,4 and 3,8 molecules. It seems, therefore, that here an analogous case is present as in the case of the complex salts derived from bivalent *iron*.

The crystals, identical in both cases, as well in habitus as in geometrical form, are *triclinic-pinacoïdal*, with the axial ratio:

$$a : b : c = 0.7193 : 1 : 0.9666;$$

$$A = 88^\circ 17'; \alpha = 80^\circ 8'$$

$$B = 100 \ 11; \beta = 104 \ 2$$

$$C = 126 \ 36; \gamma = 127 \ 47$$

Forms observed: $b = \{010\}$, large, in most cases predominant, very lustrous; $c = \{001\}$, commonly smaller than b , but in some cases broader and predominant, yielding very sharp reflections; $a = \{100\}$ and $m = \{1\bar{1}0\}$, often equally well developed, m giving better reflections than a ; $q = \{011\}$, smaller than c , yielding good reflections; $r = \{102\}$, very narrow, giving weak reflections, often absent; $s = \{0\bar{3}2\}$, mostly absent, yielding dull reflections; $p = \{120\}$, often absent, well reflecting. The habitus is either

flattened parallel to b or thick prismatic parallel to the a -axis, with $c = \{001\}$ predominant. (Fig. 3).

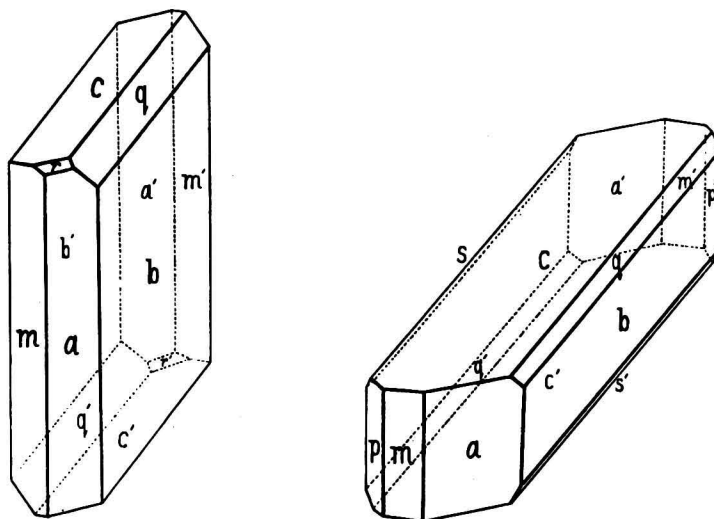


Fig. 3. Tridipyridyl-Cadmium-sulphate ($3 \text{H}_2\text{O}$).

Angular Values: *Observed:* *Calculated:*

$b : c = (0\bar{1}0) : (001) =^*$	$88^\circ 17'$	—
$c : q = (001) : (011) =^*$	50	53
$b : m = (0\bar{1}0) : (1\bar{1}0) =^*$	82	3
$m : a = (1\bar{1}0) : (100) =^*$	44	33
$a : c = (100) : (001) =^*$	79	49
$b : q = (010) : (011) =$	40	50
$a : b = (100) : (010) =$	53	24
$a : r = (100) : (102) =$	44	2
$r : c = (102) : (001) =$	35	47
$m : c = (1\bar{1}0) : (001) =$	75	48
$b : s = (0\bar{1}0) : (0\bar{3}2) =$	29	7
$s : c = (0\bar{3}2) : (001) =$	59	10
$b : p = (0\bar{1}0) : (1\bar{2}0) =$	44	30
$p : m = (1\bar{2}0) : (1\bar{1}0) =$	37	33

No distinct cleavability could be observed.

On $\{001\}$ one of the directions of optical extinction makes an angle of 9° — 10° with the edge $(001) : (010)$; on $\{010\}$ this angle is about 2° and about 12° — 13° with the edge $(010) : (110)$. On $\{001\}$ a dark branch of the hyperbola can be observed; the axial plane seems to make an angle of about 80° with the edge mentioned above.

§ 5. From a solution of equal equivalents of *cadmiumchloride* ($+2H_2O$) and *dipyridyl* immediately an insoluble, white powder is precipitated, which, on analysis, proves to be the salt: $\left\{ Cd \begin{matrix} (Dipyr) \\ Cl_2 \end{matrix} \right\}$. Analysis yielded: 33,34% *Cd*; 20,90% *Cl* and 8,23% *N*; theoretically: 33,12% *Cd*; 20,89% *Cl* and 8,25% *N*.

Also in the cases of 1 equivalent of *cadmiumchloride* with 2 or 3 equivalents of the base, the same white precipitate is formed (8,21—8,24% *N*). But in the latter case, the mother-liquor, on slow evaporation, deposited small, colourless crystals of monoclinic symmetry, which, on analysis, gave the following data: 22,03% *Cd*; 10,80% *N* and 13,82% *Cl*; theoretically, for $\left\{ Cd (Dipyr)_2 \right\} Cl_2 + 1H_2O$: 21,90% *Cd*; 10,91% *N* and 13,81% *Cl*.

The *Didipyridyl*-salt obtained crystallises from its cold, concentrated aqueous solutions in rather badly developed crystals, which are either

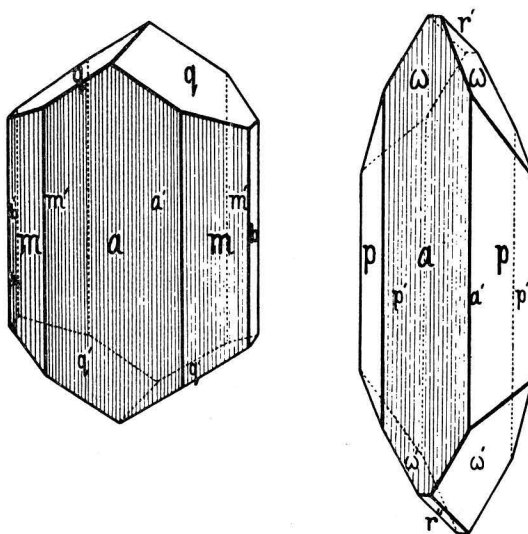


Fig. 4. Didipyridyl-Cadmium-chloride.

flat tables or thicker, prismatic individuals. In all cases, however, the principal faces yield multiple reflections; the latter are often coloured and very broad by diffraction, as a result of the fact, that the faces in the vertical zône are always striated. But also in other zônes angular deviations occur of 1° or 2° .

Monoclinic-prismatic.

$$a : b : c = 1,0173 : 1 : 0,6061 ;$$

$$\beta = 81^\circ 57'.$$

Forms observed: $a = \{100\}$, badly reflecting and vertically striated;

very broad, multiple reflections; $m = \{110\}$, yielding bad reflections, vertically striated; $b = \{010\}$, lustrous, often absent, otherwise narrow; $p = \{230\}$, well developed, yielding rather sharp reflections, often absent; $q = \{011\}$, well reflecting and relatively broad; $\omega = \{\bar{1}31\}$, often absent, when present, well reflecting; $t = \{560\}$, very narrow and badly reflecting, often absent; $r' = \{\bar{1}01\}$, very small, rather dull and often absent. The habitus is flattened parallel to $\{100\}$, more or less tabular (Fig. 4): Some crystals only exhibit the forms: a , p , ω and r , others only: a , q , m and b ; sometimes as well q , as ω are simultaneously present.

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$b : q = (010) : (011) =^*$	$59^\circ \quad 1\frac{1}{2}$	—
$a : q = (100) : (011) =^*$	$83 \quad 6$	—
$a : p = (100) : (230) =^*$	$56 \quad 30$	—
$b : m = (010) : (110) =$	$44 \quad 30$	$44^\circ \quad 37\frac{1}{2}'$
$m : p = (110) : (230) =$	ca. $10\frac{1}{2}^\circ$	$11 \quad 42\frac{1}{2}$
$a : t = (100) : (560) =$	$50 \quad 30$	$50 \quad 24$
$t : p = (560) : (230) =$	$6 \quad 0$	$6 \quad 6$
$a : \omega = (100) : (\bar{1}31) =$	$78 \quad 2$	$77 \quad 29\frac{1}{2}$
$\omega : \omega = (\bar{1}31) : (\bar{1}\bar{3}1) =$	$119 \quad 12$	$117 \quad 37$
$\omega : r' = (\bar{1}31) : (\bar{1}01) =$	$59 \quad 36$	$58 \quad 48\frac{1}{2}$
$q : q = (011) : (0\bar{1}1) =$	$61 \quad 57$	$61 \quad 57$
$a : r' = (\bar{1}00) : (\bar{1}01) =$	$66 \quad 9$	$65 \quad 16\frac{1}{2}$

No distinct cleavability could be stated.

The plane of the optical axes is $\{010\}$; on $\{100\}$ one of the axes is visible at the very border of the optical field.

In the nearest future we hope to be able to publish the results of the analogous study of the corresponding compounds of *cobaltum* and the general conclusions about the different types of complex salts, as deduced from a comparison of the data hitherto obtained.

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