

**Chemistry.** — *Complex Salts of  $\alpha$ - $\alpha'$ -Dipyridyl with Zinc and Cadmium.*  
By F. M. JAEGER and J. A. VAN DIJK.

(Communicated at the meeting of November 24, 1934).

§ 1. In a series of papers from this laboratory<sup>1)</sup> we already described a number of complex salts of bivalent *iron*, *nickel* and *copper* with  $\alpha$ - $\alpha'$ -*dipyridyl*. In the present paper the results are communicated of an analogous investigation concerning the complex ions of the same base with *zinc* and *cadmium*.

§ 2. *Zinc salts.* If to a solution of *zinc sulphate*:  $ZnSO_4 + 7H_2O$  three equivalents of *dipyridyl* are added, colourless crystals are deposited on slow evaporation in vacuo at room-temperature, which, on analysis, prove to be *tridipyridyl-zinc sulphate* +  $7H_2O$ ; found: 8,53 % Zn, 11,13 % N, and 16,66 %  $H_2O$ ; calculated: 8,64 % Zn, 11,12 % N, and 16,69 %  $H_2O$ .

The monoclinic crystals are completely isomorphous with the corresponding *nickel*- and *copper salts*.

*Monoclinic-prismatic.*

$$a : b : c = 1,5389 : 1 : 0,9132 ;$$

$$\beta = 82^\circ 13\frac{1}{2}'.$$

*Forms observed:*  $a = \{100\}$ ,  $r = \{101\}$ , and  $s = \{\bar{1}01\}$ , almost equally broad,  $\{100\}$  mostly being somewhat better developed than the others;

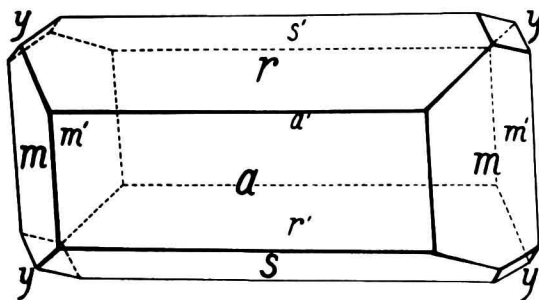


Fig. 1. Crystalform of Tridipyridyl-Zinc sulphate (+  $7H_2O$ ).

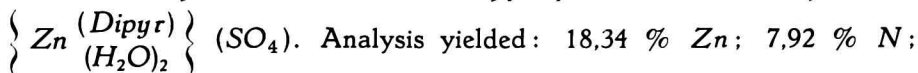
$m = \{110\}$ , rather broad and lustrous;  $y = \{011\}$ , small, but well measurable. The crystals are thick-prismatic and somewhat elongated parallel to the  $b$ -axis. (Fig. 1).

<sup>1)</sup> F. M. JAEGER and J. A. VAN DIJK, *Proceed. R. Acad. of Sciences, Amsterdam*, **37**, (1934), 10, 333, 395. In the course of these investigations attention was drawn to the remarkable fact that the special type of the possibly occurring complex ions often proves to be dependent on the specific nature of the anion of the salts used in these experiments.

Angular Values:	Observed:	Calculated:
$a : r = (100) : (101) =^*$	$53^\circ 40'$	—
$a : s = (\bar{1}00) : (\bar{1}01) =^*$	$65 \quad 11$	—
$a : m = (100) : (110) =^*$	$56 \quad 44\frac{1}{2}$	—
$r : s = (101) : (\bar{1}01) =$	$61 \quad 9$	$61^\circ 9'$
$m : m = (110) : (\bar{1}10) =$	$66 \quad 31$	$66 \quad 31$
$m : y = (\bar{1}10) : (011) =$	$51 \quad 57$	$51 \quad 58\frac{1}{2}$
$y : s = (011) : (\bar{1}01) =$	$51 \quad 14$	$51 \quad 20$
$m : s = (\bar{1}10) : (10\bar{1}) =$	$76 \quad 49$	$76 \quad 41\frac{1}{2}$
$m : r = (110) : (101) =$	$71 \quad 3$	$71 \quad 2$
$y : r = (011) : (10\bar{1}) =$	$49 \quad 17$	$49 \quad 22$
$m : y = (110) : (011) =$	$59 \quad 34$	$59 \quad 36$

No distinct cleavability was observed.

From a solution of the original zinc sulphate with *two* equivalents of dipyridyl first a white, only slightly soluble salt, crystallizing in small needles, is deposited; subsequently thick crystals of the tridipyridyl salt just mentioned can be obtained from the mother-liquor. The white, less soluble salt proves to be a *monodipyridyl* salt of the composition;



28,28 %  $(\text{SO}_4)$ ; 9,41 %  $\text{H}_2\text{O}$ ; theoretically: 18,49 % Zn; 7,92 % N; 27,17 %  $(\text{SO}_4)$ , and 10,19 %  $\text{H}_2\text{O}$ . The water is not driven out in a vacuum above sulphuric acid, but only after heating at  $150^\circ \text{C.}$ , so that, with respect to the co-ordination number *four*, it is most probable that the 2 molecules of water form part of the complex. The percentage of the  $(\text{SO}_4)$  is always a little too high, — which seems to indicate that part of the water can be substituted by  $(\text{SO}_4)$ , exactly as was observed in the case of the corresponding *iron* salt. Also from the solution of the zinc sulphate with *one* equivalent of dipyridyl this *monodipyridyl* salt is deposited. A *didipyridyl* salt seems not to be formed in aqueous solutions.

*Monodipyridyl-diaquo-zinc sulphate* crystallizes from its aqueous solutions in very small, thin monoclinic needles.

*Monoclinic-prismatic.*

$$a : b : c = 1,217 : 1 : 0,531 ;$$

$$\beta = 77^\circ 5'.$$

*Forms observed:*  $a = \{100\}$ , broader than  $m = \{110\}$ ;  $q = \{011\}$ , all

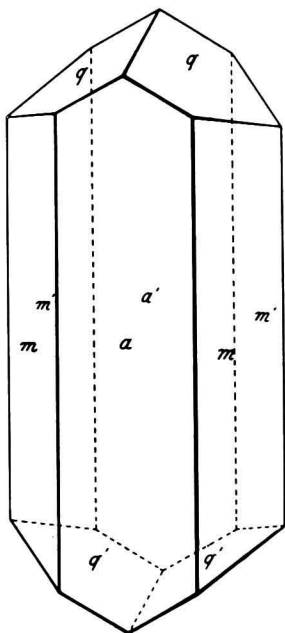


Fig. 2. Crystalform of Monodipyridyldiaquo-Zinc sulphate.

yielding sufficiently sharp reflections. The crystals are prismatic, with their elongation in the direction of the *c*-axis.

<i>Angular Values:</i> <sup>1)</sup>	<i>Observed:</i>	<i>Calculated:</i>
$a:m = (100):(110) =$	$49^\circ 52'$	—
$m:q = (110):(011) =$	$61 \quad 22$	—
$m:q = (\bar{1}10):(011) =$	$77 \quad 6$	—
$q:q = (011):(0\bar{1}1) =$	$54 \quad 44$	$54^\circ 42'$
$a:q = (100):(011) =$	$78 \quad 28$	$78 \quad 33$
$m:m = (110):(\bar{1}10) =$	$80 \quad 16$	$80 \quad 16$

A distinct cleavability could not be stated.

On {100} an axial image may be occasionally observed; the plane of the optical axes is {010}, the first bissectrix being almost perpendicular to {100}. Strong, inclined dispersion.

§ 3. The same experiments now were made, *zinc chloride* being used instead of the sulphate.

From the solution of 1 mol. (*zinc chloride* +  $1\frac{1}{2}H_2O$ ) + 1 mol. *dipyridyl* a colourless salt crystallizes in the shape of intergrown, irregularly bordered needles; its solubility is about the same as, or at least comparable with, that of the *tridipyridyl* salt to be described later on.

Analysis yielded: 22,31 % *Zn* (in the anhydrous salt); 9,41 % *N*; no loss of water, even at 150° C., occurred; for the *monodipyridyl-zinc-chloride*:  $\left\{ \begin{matrix} Zn \\ Cl_2 \end{matrix} \right\}^{(Dipyr)}$  is calculated: 22,36 % *Zn* (in the anhydrous salt); 9,58 % *N*.

The salt is more soluble than the corresponding *cupric* salt formerly described. It may be that also a *monodipyridyl* salt with two molecules of water can exist.

§ 4. From a solution of *zinc chloride* to which 2 or 3 equivalents of *dipyridyl* are added, flat colourless crystals of the *tridipyridyl-zinc-chloride* are deposited. They crystallize with 7 molecules of water, as may be seen from the following data:

On analysis they yielded: 9,05 % *Zn*, 11,30 % *N*, and 17,47 %  $H_2O$ ; theoretically: 8,95 % *Zn*; 11,50 % *N*, and 17,25 %  $H_2O$ .

*Tridipyridyl-Zinc-Chloride*:  $\{Zn (Dipyr)_3\} Cl_2 + 7 H_2O$ , crystallizes from its aqueous solutions in small, strongly refracting, colourless crystals or parallelogram-shaped, thin plates.

*Monoclinic-prismatic.*

$$a : b : c = 0,6304 : 1 : 2,1051 ;$$

$$\beta = 72^\circ 43'.$$

*Forms observed*:  $c = \{001\}$ , predominant and very lustrous;  $m = \{110\}$ ,

<sup>1)</sup> These values were measured by means of the bicircular goniometer by Mr. W. J. VAN WEERDEN, candidate of chemistry at this laboratory.

yielding very sharp reflections;  $q = \{011\}$ , small, but very well measurable;  $a = \{100\}$ , very narrow, yielding feeble reflections; sometimes very

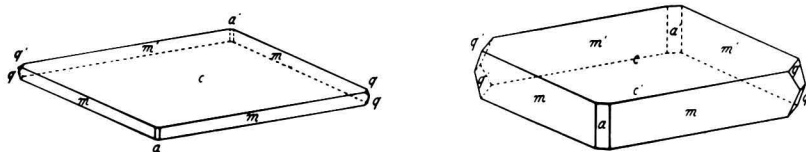


Fig. 3. Crystalforms of Tridipyridyl-zinc-chloride.

narrow,  $\omega = \{118\}$  and  $\varepsilon = \{115\}$ , dull and only approximately measurable. The crystals are flattened parallel to  $\{001\}$ .

Angular Values:	Observed:	Calculated:
$c : m = (001) : (110) =^*$	$75^\circ 5'$	—
$c : q = (001) : (011) =^*$	$63 33$	—
$m : m = (110) : (1\bar{1}0) =^*$	$59 54$	—
$m : q = (110) : (011) =$	$55 24$	$55^\circ 39'$
$m : a = (110) : (100) =$	$29 57$	$29 57$
$a : c = (100) : (001) =$	$72 53$	$72 43$
$c : \omega = (001) : (118) =$	$22 45$	$22 30$
$c : \varepsilon = (001) : (115) =$	ca. $33^\circ$	$31 53$

No distinct cleavability was observed.

The plane of the optical axes is perpendicular to  $\{010\}$  and practically perpendicular to  $\{001\}$ , so that the normal on  $\{001\}$  is the first bissectrix, probably of positive character, although the birefringence is so weak that no accurate determination is possible. The apparent axial angle is rather small, about of medium size; the dispersion is strong:  $\rho < \nu$  and has an apparently rhombic character.

Evidently only the *mono-* and *tridipyridyl* salts are formed in the case of zinc *chloride*, — exactly as in the case of the corresponding *sulphate*.

§ 5. *Cadmium salts.* Solutions of *cadmium nitrate* were mixed with 1, 2 or 3 equivalents respectively of dipyridyl and slowly evaporated at room-temperature. The solution containing 3 molecules of dipyridyl yielded long, slightly soluble, colourless needles, which, on analysis, proved to correspond to a *di-dipyridyl* salt of the composition:  $\{Cd (Dipyr)_2\} (NO_3)_2 + \frac{1}{2} H_2O$ ; found: 20,15 % Cd, 14,98 % N and 1,62 %  $H_2O$ ; calculated: 20,16 % Cd, 15,07 % N, and 1,62 %  $H_2O$ .

From the mother-liquor the corresponding *tri-dipyridyl-cadmiumnitrate*:  $\{Cd (Dipyr)_3\} (NO_3)_2 + 7 H_2O$  crystallizes, as was proved by analysis: 13,67 % Cd, 13,64 % N, 15,12 %  $H_2O$ ; theoretically: 13,53 % Cd, 13,47 % N, and 15,18 %  $H_2O$ . The crystals soon lose their water of crystallization when exposed to the air.

Also from a solution of the nitrate with 2 equivalents of dipyridyl, the *di-dipyridyl* salt just mentioned is primarily deposited; however, from the mother-liquor later on colourless rhombic crystals are deposited, which

have the same composition and which — as far as the very badly developed needles first mentioned allowed a measurement by means of the bicircular goniometer — seem to have also the same crystallographical form as the needles of the didipyridyl salt mentioned above.

Finally from a solution of cadmium nitrate + 1 equivalent of dipyrldyl colourless, lustrous crystals are formed, which proved to be  $\left\{ \begin{array}{l} Cd (Dipyr) \\ (H_2O)_2 \end{array} \right\} (NO_3)_2$ ; they already lose their water in vacuo at room-temperature. The crystals commonly are badly developed and often show curved faces. On analysis they proved to contain: 26,40 % Cd; 13,03 % N, and 8,10 %  $H_2O$ ; theoretically: 26,23 % Cd, 13,07 % N, and 8,40 %  $H_2O$ .

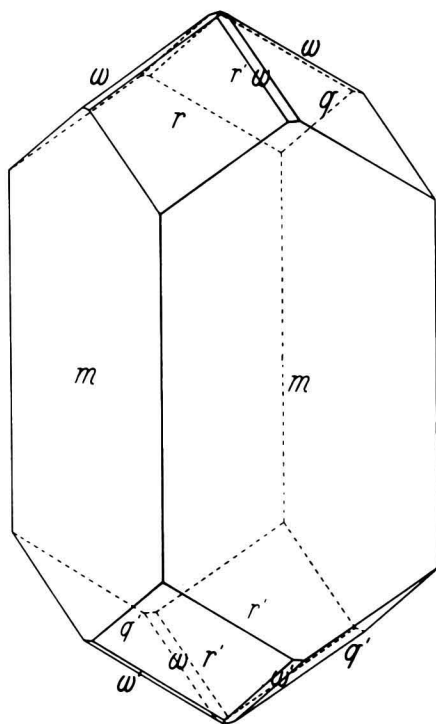


Fig. 4. Crystalform of Tridipyridyl-cadmium nitrate.

§ 6. *Tridipyridyl-Cadmiumnitrate*:  $\{Cd (Dipyr)_3\} (NO_3)_2 + 7H_2O$  crystallizes in small, rather isometrically developed crystals, which soon become opaque, so that rapid measurements have to be made. The crystals are badly built: in the zone  $m:r:q:m$  the angular values are appreciably oscillating, the differences for the same angles amounting from  $1^\circ$  to  $4^\circ$ , and in the zone  $m:m$  from  $1^\circ$  to  $2^\circ$ .

*Rhombic-bipyramidal.*

$$a : b : c = 0,9011 : 1 : 0,8232.$$

The forms observed are:  $m = \{110\}$ , broad, well reflecting;  $r = \{101\}$  and  $q = \{011\}$ , about equally large, often yielding dull reflections;  $\omega = \{112\}$ , very small,

sometimes absent. The habitus of the crystals is thick-prismatic, occasionally elongated parallel to the  $c$ -axis.

Angular Values:	Observed:	Calculated:
$m : m = (110) : (\bar{1}10) =^*$	$84^\circ 3'$ ( $83^\circ 30' - 84^\circ 30'$ )	—
$m : r = (110) : (101) =^*$	$59 56$ ( $59^\circ - 61^\circ$ )	—
$r : q = (101) : (011) =$	$55 48$ ( $53^\circ 30' - 57^\circ 30'$ )	$55^\circ 15'$
$q : m = (011) : (\bar{1}10) =$	$64 16$ ( $63^\circ 40' - 65^\circ 30'$ )	$64 49$
$r : \omega = (101) : (112) =$	$27 18$ ( $26^\circ 30' - 28^\circ 30'$ )	$26 46\frac{1}{2}$
$\omega : q = (112) : (011) =$	$28 30$ ( $28^\circ - 29^\circ 30'$ )	$28 28\frac{1}{2}$

No distinct cleavability was observed.

Here the remarkable fact can be stated that in its habitus as well as in its angular values, this salt shows a complete analogy, not discernible from real isomorphism, with:  $\{Fe(Dipyr)_3\}Cl_3 + 7H_2O$ ; i.e. an isomorphism appears to exist here between a *nitrate* and a *chloride* of the same type.

Solutions of both salts were mixed in very different proportions and left to crystallize at room-temperature. In all cases only red, completely homogeneous mixed crystals were deposited, so that the perfect miscibility of the two compounds in the solid state is proved beyond all doubt.

§ 7. *Didipyridyl-Cadmiumnitrate*:  $\{Cd(Dipyr)_2\}(NO_3)_2 + \frac{1}{2}H_2O$  is rhombic. On slow evaporation of the solution at room-temperature the salt crystallizes in big, flat colourless plates, with hexagonal boundaries.

They are rhombic-bipyramidal, with:

$$a : b : c = 1,2283 : 1 : 1,2034.$$

Forms observed:  $o = \{122\}$ , very lustrous and well developed as terminal faces of the elongated tables;  $a = \{100\}$ , predominant, vertically striated and yielding bad and multiple reflections;  $m = \{110\}$ , narrow, mostly dull and often striated;  $b = \{010\}$ , narrow, but very lustrous.

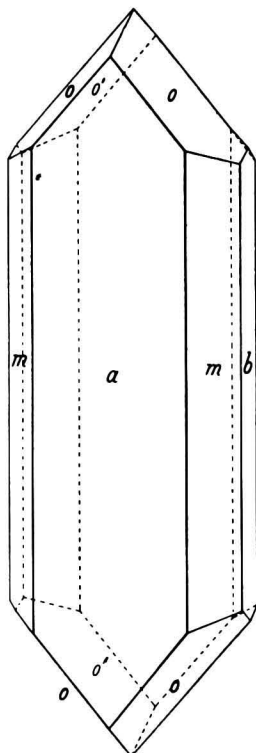


Fig. 5. Crystalform of Didipyridyl-Cadmium nitrate.

Angular Values:	Observed:	Calculated:
$o : o = (122) : (\bar{1}\bar{2}\bar{2}) =$	$94^\circ 27'$	—
$o : o = (122) : (\bar{1}2\bar{2}) =$	$34 46$	—
$o : b = (122) : (010) =$	$42 45$	$42^\circ 46\frac{1}{2}'$
$a : o = (100) : (122) =$	$72 37$	$72 37$
$a : m = (100) : (110) =$	$50 38$	$50 51$
$m : b = (110) : (010) =$	$39 22$	$39 9$

No distinct cleavability was found; perhaps one parallel to  $b$  is present.

On the faces of the vertical zone the optical extinction is perpendicular to the  $c$ -axis. The plane of the optical axes is  $\{001\}$ , with  $a$  as the first, positive bissectrix. The apparent axial angle is rather small; strong dispersion.

The fine needles first separated out from the solutions of cadmium nitrate and 2 equivalents of dipyridyl were measured by Dr. TERPSTRA by means of the bicircular goniometer. The crystals are so small and so badly developed that it appeared hardly possible to decide whether they are monoclinic or rhombic: in the latter case their axial ratio must approximately be:  $a : b : c = 2,6 : 1 : 1,28$ , with the forms:  $\{100\}$  and  $\{111\}$

and with {001} as the plane of the optical axes, the  $a$ -axis being the first, positive bissectrix. If we take into account that the pyramid of the thicker crystals described above really is {122}, so that the approximate axial ratio of the needles then would become:  $a : b : c = 1,3 : 1 : 1,28$ , that moreover, the optical properties of the latter are completely analogous to those of the big crystals, and that the chemical composition also is the same, — then it seems allowable to conclude from this evidence that the two preparations are *identical*.

§ 8. The *Mono-dipyridyl-Cadmium nitrate*:  $\left\{ \begin{array}{l} Cd \text{ (Dipyridyl)} \\ (H_2O)_2 \end{array} \right\} (NO_3)_2$   
crystallizes in aggregates of thin, rectangularly shaped plates of monoclinic symmetry; the individual crystals are very lustrous and yield sharp reflections, but gradually they become opaque.

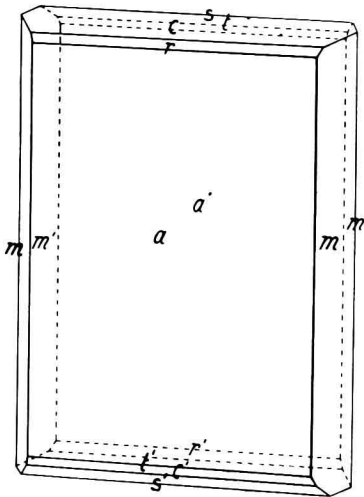


Fig. 6.

*Monoclinic-prismatic.*

$$a : b : c = 2,5505 : 1 : 1,6981 ;$$

$$\beta = 74^\circ 14'.$$

*Forms observed*:  $a = \{100\}$ , predominant and very lustrous;  $m = \{110\}$  and  $c = \{001\}$ , about equally broad and yielding very sharp reflections;  $r = \{101\}$ , somewhat narrower than  $s = \{101\}$ , both very well reflecting;  $t = \{305\}$ , often absent, sometimes only present with  $a$ ,  $m$ , and  $c$ . The habitus of the crystals is tabular parallel {100}, with a slight elongation in the direction of the  $c$ -axis. (Fig. 6).

Angular Values:	Observed:	Calculated:
$a : m = (100) : (110) = *$	67° 50'	—
$a : r = (100) : (101) = *$	45 45	—
$r : c = (101) : (001) = *$	28 29	—
$m : m = (110) : (\bar{1}10) =$	44 20	44° 20'
$c : s = (001) : (\bar{1}01) =$	37 52	38 2
$s : a = (\bar{1}01) : (\bar{1}00) =$	67 54	67 44
$c : t = (001) : (\bar{3}05) =$	56 52	56 48 $\frac{3}{4}$
$c : m = (001) : (110) =$	84 7	84 7
$m : r = (110) : (101) =$	74 48	74 44
$m : s = (\bar{1}10) : (\bar{1}01) =$	81 45	81 46 $\frac{1}{2}$

No distinct cleavability was observed.

On {100} normal extinction, on {110} under a small angle with the direction of the *c*-axis.

In the near future we hope to be able to communicate the results obtained with some other *cadmium* salts of this type.

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

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**Chemistry.** — *Isomerism of the cyclic isoprene sulphones.* By J. BÖESEKEN and E. DE ROY VAN ZUYDEWIJN.

(Communicated at the meeting of November 24, 1934).

On the ground of theoretical considerations INGOLD and ROTHSTEIN (Journ. Chem. Soc. **1929**, 8) concluded that strongly positive groups, such as  $\text{—NR}_3^+$  and  $\text{—SO}_2\text{R}^{+-}$ , in the presence of KOH, are able to activate a potentially mobile three-carbonsystem, to which they are attached. They demonstrated it for the first group; in unsaturated sulphones of the type R-SO<sub>2</sub>-propenyl this did not succeed, owing to linkage of H-OH to the double bond (Journ. Chem. Soc. **1934**, 684).

It is to be expected, therefore, that the transposition of the cyclic isoprene-sulphone in alkaline solution under the influence of ultraviolet light, found by EIGENBERGER (Journ. prakt. Chem. [2], **129**, 312 (1931)), of which we already pointed out the improbability of a cis-trans conversion (Rec. trav. chim. **53**, 673 (1934)), is a tautomeric transposition. In that case not the application of ultraviolet rays, but KOH would be essential to the transposition; indeed also after ten days *in the dark* the cyclic isoprene sulphone dissolved in 0.5 n KOH is for a considerable part converted into its isomer. The light only has an accelerating effect. Whereas in isoprene sulphone the equilibrium appears to be situated far to the side of the isomer, we found as the result of some preliminary observations that this is not the case in the cyclic sulphone of butadiene. Either by exposure to light or by simply leaving a solution in 0.5 n KOH for some days, from the butadiene sulphone melting at 63°, regularly an oil is formed which does not set even in ice and salt.

The decomposition at 180° of the ordinary butadiene sulphone was made use of in order to separate it from the formed stabler isomer. A substance was left behind which is a solid at the usual temperature (meltingpoint 45—50°) and could be distilled without decomposition in the cathode-vacuum (yield about 1/3 of the original sulphone). On rubbing together this isomer with the original substance, we again obtained a non-setting oil.