Chemistry. — *The Crystalforms of Some Complex Salts of Triaminopropane with trivalent Cobaltum and Rhodium.* By P. TERPSTRA and J. TER BERG. (Communicated by Prof. F. M. JAEGER).

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§ 1. In the following we communicate the results of the crystallographical study of a series of complex salts of *triaminopropane*: $CH_2(NH_2).CH(NH_2).CH_2(NH_2)$ of the general type $\{Me(tpn)_2\}X_3$, in which $Me = Co^{\cdots}$ or $Rh^{\cdots}$, whilst $X = Cl$, Br, J or SCN. Salts of this type were first prepared by POPE and MANN [1]). Besides the salts mentioned, which all could be obtained in beautiful crystals, we also studied the crystalform of the hydrochloride of *triaminopropane* itself, which crystallizes with $1\,H_2O$.

In general these salts were prepared after the method indicated by MANN and POPE (loco cit.) by dissolving 5 grammes of the hydrochloride: $C_3H_{11}N_3, 3HCl + H_2O$ in a solution of 2 grammes of $NaOH$ in 25 cm³ of water and heating this at a reflux-cooler on the waterbath during 10 hours with 2 grammes of *monochloro-pentammino-cobaltic-chloride* or with the corresponding quantity of *monochloro-pentammino-rhodium-chloride* [2]). The solution obtained then was filtered off and left standing for crystallisation: after some days small crystals were deposited which, on analysis, proved to have the composition: $\{Co(tpn)_2\}Cl_3$ or $\{Rh(tpn)_2\}Cl_3$ respectively. The corresponding *bromides*, *iodides* and *rhodanides* were prepared by treating the *chlorides* with a concentrated solution of $NaBr$, NaI or $KCNS$. After recrystallisation from water, the salts mentioned all proved to be deposited in measurable crystals of the anhydrous compounds.

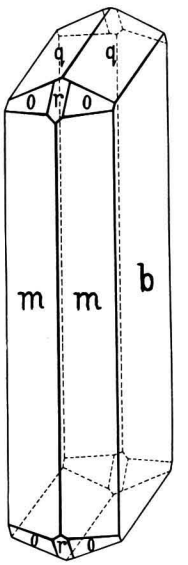

Fig. 1. *Crystalform of Triaminopropane-hydrochloride* $(+\,1H_2O)$.

§ 2. *Triaminopropane-hydrochloride-monohydrate* crystallizes over sulphuric acid from its aqueous solution in colourless, flattened needles or prisms (Fig. 1).

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[1]) F. G. MANN and W. J. POPE, Proceed. R. Soc. London, A, **107**, 80, (1925); Journ. Chem. Soc. (1926) 2675.

[2]) S. M. JÖRGENSEN, Zeits. f. anorg. Chem., **5**, 369, (1894); C. CLAUS, Journ. f. Prakt. Chem., **63**, 99, (1854).

Rhombic-bipyramidal.

$a : b : c = 0{,}510 : 1 : 0{,}488.$

Forms observed: $m = \{110\}$ and $b = \{010\}$, large; $q = \{011\}$, well developed; $o = \{111\}$ and $r = \{101\}$ small, commonly present with only a part of their planes. The crystals are flattened parallel to $\{010\}$ and elongated in the direction of the *c*-axis.

Angular Values:	*Observed*:	*Calculated*:
$b : m = (010) : (110) =$	*62° 58′	—
$b : o = (010) : (111) =$	*70 34	—
$r : r = (101) : (\bar{1}01) =$	87 26	87° 28′
$m : o = (110) : (111) =$	43 1	42 57
$b : q = (010) : (011) =$	63 50	63 59
$q : o = (011) : (111) =$	40 46	40 41

Optically biaxial, with $\{001\}$ as the plane of the optical axes and the *b*-axis as first bissectrix of negative character. The apparent axial angle $2V$ is 77°. No piezo-electricity was observed.

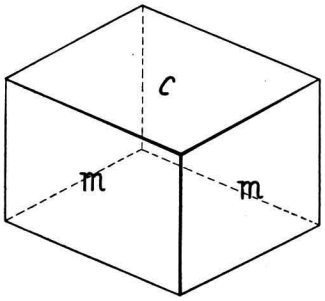

Fig. 2. *Crystalform of* $\{Co\,(tpn)_2\}Cl_3$.

§ 3. *Cobaltic Salts.*

1. *Di-triaminopropane-cobaltic-chloride* crystallizes from its aqueous solutions in rhombohedrally-shaped crystals (Fig. 2).

Monoclinic-prismatic.

$a : b : c = 1{,}522 : 1 : 1{,}819;$
$\beta = 63° 9'.$

Forms observed: $m = \{110\}$ and $c = \{001\}$, about equally large; $R = \{\bar{1}01\}$, rarely present and only very small.

Angular Values:	*Observed*:	*Calculated*:
$m : m = (110) : (1\bar{1}0) =$	*107° 14′	—
$m : c = (110) : (001) =$	*74 28	—
$c : R = (001) : (\bar{1}01) =$	*66 38	—
$m : R = (110) : (\bar{1}01) =$	112 24	112° 28′

Geometrically the crystals are pseudo-rhombohedral.

Optically biaxial, with $\{010\}$ as the axial plane; one optical axis strongly excentrically emerges on $\{001\}$. The optical character is negative. The crystals melt at 310° C. under decomposition; their specific gravity is: 1.680.

2. *Di-triaminopropane-cobaltic-bromide.*

Also this salt crystallizes in small, red-brown crystals, which are perfectly isomorphous with those of the chloride. The form $R=\{\bar{1}01\}$ was here, however, well developed and the habitus was elongated in the direction of the *c*-axis (Fig. 3).

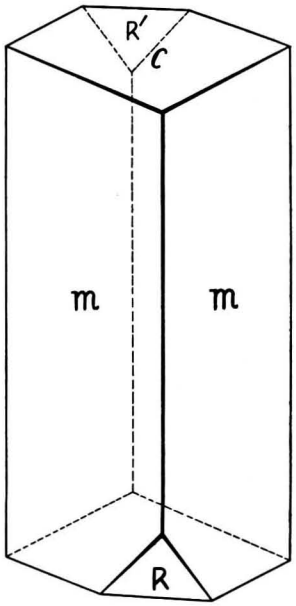

Fig. 3. *Crystalform of* $\{Co(tpn)_2\}Br_3$.

Monoclinic-prismatic.

$$a:b:c=1.522:1:1.780$$
$$\beta=61°36'.$$

Forms observed: $m=\{110\}$, $c=\{001\}$ and $R=\{\bar{1}01\}$.

Angular Values:	*Observed*:	*Calculated*:
$m:m=(110):(1\bar{1}0)=$	*106° 30′	—
$m:c=(110):(001)=$	*73 28	—
$c:R=(001):(\bar{1}01)=$	*66 39	—
$m:R=(110):(\bar{1}01)=$	111 48	111° 52′

Optically biaxial, with $\{010\}$ as the axial plane; one axis very excentrically emerges on $\{001\}$. The double refraction is negative. The crystals melt, under decomposition, at 322°C.; their specific gravity is: 2.165.

3. *Di-triaminopropane-cobaltic-iodide.*

Whilst the *chloride* and *bromide* mentioned obviously manifested a pseudo-trigonal form, the *iodide* is really rhombohedral and truly uniaxial.

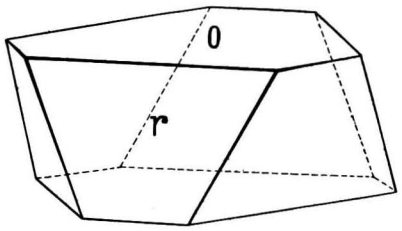

Fig. 4. *Crystalform of* $\{Co(tpn)_2\}I_3$.

On slow evaporation ditrigonal crystals are deposited, having the form of Fig. 4, which closely resemble flattened octahedra. The crystals are badly measurable because of they having cracked planes and often being aggregated in big, star-like clusters. Better crystals were obtained by cooling a hot, saturated solution: they then look as thin, hexagonal tables parallel to $\{0001\}$.

A LAUE-pattern perpendicular to $\{0001\}$ showed a trigonal axis and three planes of symmetry passing through this axis. The possible space-groups are: C_{3V}, D_3m or D_{3D} (SCHOENFLIES).

As no piezo-electricity nor an optical rotation were observed, they most probably belong to the group D_{3D}.

Ditrigonal-scalenohedral.

$$a:c=1:2.962.\ (\alpha=51°\ 52').$$

Forms observed: $o = \{111\}$ (trigonal axes) $= \{0001\}$ and $r = \{100\} = \{10\bar{1}1\}$.

Angular Values:	*Observed*:	*Calculated*:
$o : r = (111) : (100) =$	*73° 42′	—
$r : r = (100) : (010) =$	112 24	112° 26′

The crystals are uniaxial, positive.

They melt at 332° C. under decomposition; their specific gravity is; 2.552.

4. *Di-triaminopropane-cobaltic-rhodanide.*

The salt crystallizes from its aqueous solutions in red-brown, strongly pleochroitic crystals with rather oscillating angular values.

Triclinic-pinacoidal.

$a : b : c = 1.882 : 1 : 1.691$;

$A = 93° 44\frac{2}{3}'$; $\alpha = 93° 59'$.
$B = 123 \ 42\frac{2}{3}$; $\beta = 123 \ 44$.
$C = 90 \ 46\frac{2}{3}$; $\gamma = 88 \ 26$.

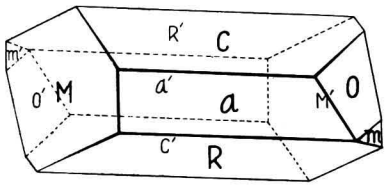

Fig. 5. *Crystalform of* $\{Co\,(tpn)_2\}\,(SCN)_3$.

Forms observed: $R = \{\bar{1}01\}$; $a = \{100\}$ and $c = \{001\}$, all about equally well developed; $M = \{1\bar{1}0\}$ and $O = \{111\}$, rather large; $m = \{110\}$, small. The crystals are prismatic with an elongation in the direction of the *b*-axis (Fig. 5).

Angular Values:	*Observed*:	*Calculated*:
$a : c = (100) : (001) =$	*56° 17$\frac{1}{3}$′	—
$c : R = (001) : (\bar{1}01) =$	*57 1	—
$a : O = (100) : (111) =$	*48 14	—
$[z_c] : [z_b] = [001] : [010] =$	*93 59	—
$[z_b] : [z_q] = [010] : [0\bar{1}1] =$	*55 23	—
$a : m = (100) : (110) =$	56 25	56° 20′
$a : M = (100) : (1\bar{1}0) =$	54 50	54 46
$R : M = (101) : (1\bar{1}0) =$	106 23	106 31
$[z_b] : [z_o] = [010] : [111] =$	57 55	58 12

§ 4. *Rhodiumsalts.*

1. *Di-triaminopropane-rhodium-chloride.*

Although this salt and the other *rhodium*salts do not crystallize as well as the corresponding cobaltic salts, yet they could fairly well be measured. Their habitus is exactly the same as that of the cobaltic salts; they are with the latter perfectly isomorphous.

The *chloride* is *monoclinic-prismatic*, with: $a : b : c = 1.512 : 1 : 1.840$ and $\beta = 64° 6'$. The *forms observed* are: $m = \{110\}$, $c = \{001\}$ and $R = \{101\}$. The crystals are quite analogous to those in Fig. 3.

Angular Values:	*Observed*:	*Calculated*:
$m : m = (110) : (1\bar{1}0) =$	*107° 20′	—
$m : c = (110) : (001) =$	*75 0	—
$c : R = (001) : (\bar{1}01) =$	*66 51	—
$m : R = (110) : (\bar{1}01) =$	112 40	112° 51′

Optically biaxial, with $\{010\}$ as the axial plane; the optical character is negative.

2. *Ditriaminopropane-rhodium-bromide.*

The crystals are *monoclinic-prismatic*, with: $a : b : c = 1.518 : 1 : 1.786$ and $\beta = 61° 58'$.

Forms observed: $m = \{110\}$, $c = \{001\}$ and $R = \{\bar{1}01\}$; the habitus is that of Fig. 3.

Angular Values:	*Observed*:	*Calculated:*
$m : m = (110) : (1\bar{1}0) =$	*106° 30′	—
$m : c = (110) : (001) =$	*73 40	—
$c : R = (001) : (\bar{1}01) =$	*66 44	—
$m : R = (110) : (\bar{1}01) =$	111 52	111° 58′

Optically biaxial; $\{010\}$ is the plane of the optical axes; the double refraction is negative.

3. *Di-triaminopropane-rhodium-iodide.*

Only very small crystals proved to be sufficiently well measurable: on further growth they get dull and rough, so that they no longer yield good reflections. The crystals are rigorously isomorphous with those of the corresponding cobaltic salt (Fig. 4).

Ditrigonal-scalenohedral.

$a : c = 1 : 3{,}004$. $(\alpha = 51° 16')$.

Forms observed: $o = \{111\} = \{0001\}$; $r = \{100\} = \{10\bar{1}1\}$.

Angular Values:	*Observed*:	*Calculated*:
$o : r = (111) : (100) =$	*73° 55′	—
$r : r = (100) : (010) =$	112 30	112° 38′

Optically uniaxial, positive.

The specific gravity is: 2,680.

An *X*-ray-investigation of the salts described will soon be published.

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