

**Chemistry.** — “*Complex Boric-Acid Compounds and the Optically Active Boron Atom*”. By Prof. J. BÖESEKEN and J. MEULENHOF.

(Communicated at the meeting of January 29, 1924).

In a communication in these proceedings on the „valency of boron”<sup>1)</sup> some compounds were mentioned of boric acid with pyrocatechine both with aliphatic and aromatic hydroxy acids, which have been described more fully by Mr. P. H. HERMANS<sup>2)</sup>. Their constitution can be brought in symbol in the simplest way by the assumption that the boron atom with *four* valencies was bound to two molecules of the organic poly oxy compound, thus forming a monovalent anion:

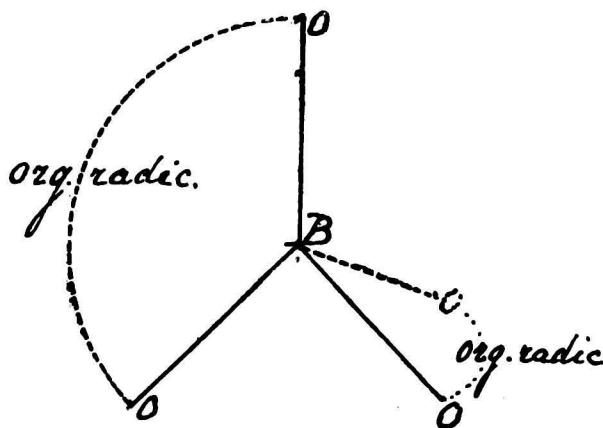


Fig. 1.

In order to get a closer confirmation of this view a number of new compounds of this type were prepared synthetically, and it was tried to furnish the definitive proof of this constitution by effecting the splitting up into optical antipodes of a derivative, the anion of which cannot coincide with its mirror image.

This is the case with the borosalicylates, where we have to do with the optically-active spirane compound, as can be easily derived from the adjoined symbol (next page).

<sup>1)</sup> These Proceedings 26, 97 (1923)

<sup>2)</sup> These Proceedings 26, 32 (1923).

As regards the first part of this task, besides the potassium salt already described, the following salts were prepared and analysed: ammonium-, aniline-, parachloraniline, dimethylaniline-, and pyri-

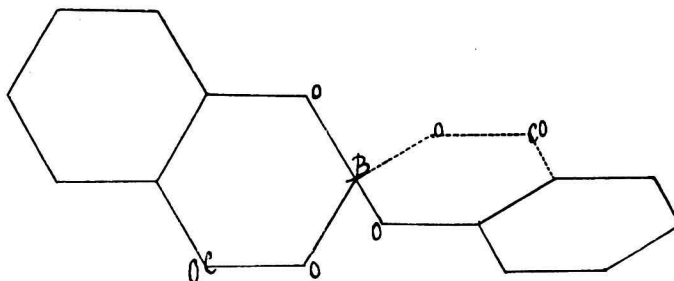
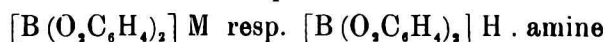


Fig. 2.

dine salt of the dipyrocatechine boric acid; besides by careful heating, the free acid was prepared from the aniline salt; it appeared to be undecomposed volatile.

All these salts have the composition:



and crystallized without crystal water. The ammonium salt was undecomposed volatile; from the aniline salt the acid was obtained which had the concentration  $[B(O_2C_6H_4)_2] H$ .

Further the aniline and pyridine salts of dipyrogallool boric acid were prepared; as further salts of this acid did not readily crystallize, no further attempts were made to obtain optical antipodes, which are theoretically possible.

Then the influence on the conductivity of boric acid was determined for the two nitro pyrocatechines 1.2.3 and 1.2.4, which was very great: for  $1/10$ , normal to  $1/2$ , mol.  $H_3BO_3$ , at  $25^\circ$  of 1.2.3 =  $1163 \times 10^{-6}$  Kohlrausch-Holborn-units, for 1.2.4 =  $302 \times 10^{-6}$ .

What is remarkable here is the much stronger action of the nitro-group in the ortho-position, which will very likely be due for the greater part to the more strongly acid character of the nitro pyrocatechine part in the boro-complex. In pyro catechine itself this increase of the conductivity amounted to = 137.2 for the same concentration.

Potassium-, ammonium, and aniline salts of di-(3 nitropyrocatechine) boric acid were prepared and analysed; they crystallized without water of crystallisation; attempts to prepare the free complex acid from the aniline salts by distilling the aniline away, did not succeed, as aniline did not escape until a temperature was reached at which decomposition set in. Also of the isomer 4 nitropyrocatechine-boric

acid the corresponding salts were obtained, which like those of the isomer crystallized without crystal water. The constitution was  $[B(O_2B_2H_2NO_2)_2]R$ .

Though these nitropyrocatechine borates might be used for the splitting up into optical isomers, we have preferred to take boro salicylic acid for this purpose, in view of the lengthy process of preparation of larger quantities of the nitropyrocatechines. Experience had taught us that the complex boro-salts of this acid crystallized exceedingly well; besides the acid itself is accessible in unlimited quantities.

First a number of salts was prepared. In anhydrous condition all of them had the constitution  $[B(O_2COC_6H_4)_2]R$ , in which R represents one equivalent of a base.

The aniline-, ammonium-, potassium-, sodium-, silver salts crystallized without water of crystallisation, the pyridine salt with one molecule. The salts of zinc, copper, cobalt, manganese<sup>II</sup>, nickel, magnesium, and calcium were very fine, they all crystallized with *ten* molecules of water of crystallisation and are probably isomorphous.

The colour of copper-, cobalt, and manganese salts differed from that of the anhydrous anorganic salts. Copper salt was light *green*, cobalt salt salmon-coloured, manganese salt light *yellow*. This and the fact that heterogenous metals, as copper and calcium, range themselves with zinc and manganese, makes it probable that the great anion constitutes here the formative part of the salt, and that the water molecules probably from part of this anion.

The strontium-, barium-, and lead salts agree with each other as regards form and the absence of water of crystallisation.

With regard to the splitting up of the boro-salicylic acid in the optically active components, we have succeeded in showing the asymmetry of the anion in the *strychnine salt* with certainty.

This was obtained from very diluted aqueous-alcoholic solutions in rodlike crystals or in more felty needles.

In fractionated crystallisation the different fractions appeared to have the same constitution as the salts with organic bases described, only the rotations differed, e.g.  $+14^\circ.5$ ,  $0^\circ$ ,  $-7^\circ.6$ , and  $-11^\circ.9$ .

By shaking with  $CHCl_3$ , a preparation  $[\alpha]_D = +22^\circ.6$  was obtained from the dextro-rotatory fraction; as salicylic acid-strychnine and the base itself, the latter either in the presence of boric acid or not, are laevo-rotatory or feebly dextro-rotatory ( $[\alpha]_D = +2^\circ.5$ ) in chloroformic solution, the proof of the activity of the anion had been given by this.

This salt, which evidently is more sparingly soluble than the laevo-rotatory isomer, is consequently the *d'l-strychnine-borosalicylate*.

If the solution of this salt in  $CHCl_3$  was dried with  $CaCl_2$ , the rotatory

power diminished, becoming laevo-rotatory after some time, and finally constant at  $-13^{\circ}.3$ . Inversely a laevo-rotatory fraction was reduced to the same value. That this was the consequence of traces of water, was proved as follows: if the solvent was dried with  $P_2O_5$ , the rotatory power also diminished, but much more slowly. In a check experiment with the same positive-rotatory preparation  $[\alpha]_D = +11^{\circ}.2$ , hence a mixture with an excess of d'l, one specimen dissolved in  $CHCl_3$  dried on  $CaCl_2$ , another specimen in the same solvent dried on  $P_2O_5$ , the former had reached the final rotation  $[\alpha]_D = -13^{\circ}.3$  already after seven days, the latter after three weeks.

We see accordingly that traces of  $H_2O$  effect a racemation, which is to be expected here, as the borosalicylic acid salts in  $H_2O$  are partially hydrolyzed, and are then, of course, very rapidly racemized. Also with brucine similar phenomena were observed; fuller information will be given in the thesis for the doctorate of Mr. MEULENHOF.

*Delft, January 1924.*

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