

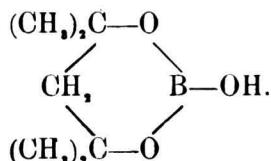
Chemistry. — “*The Valency of Boron*”. By Prof. J. BÖSEKEN.

(Communicated at the meeting of December 30, 1922).

As the complex organic boric acid compounds have gradually acquired a great significance for the determination of the composition of a number of organic compounds and for the knowledge of the configuration and of the state of motion of the molecules in space, it was felt as a serious deficiency that the existence of these complex compounds had so far been exclusively derived by an indirect way, and that no compound had as yet been separated, the composition of which had been entirely made clear.

Some years ago we had, indeed, succeeded¹⁾ in obtaining some well crystallized salts of pyrocatechol boric acid, but they seemed to be built up in such a complicated way that no accurate conception could be formed of their composition.

Now it chanced that Mr. HERMANS²⁾, who was engaged in an investigation of the equilibria in the system glycol + acetone \gtrless glycol acetone + H₂O, and also examined the behaviour of the glycols towards boric acid, obtained a compound that crystallized beautifully from tetra-methyl-propane-diol-1.3 and boric acid, which according to analysis and properties possessed the following cyclic composition :



Against our expectation this compound, which had a delicate saffron odour, was hardly acid, at any rate less acid than boric acid itself, as a solution of this substance had a smaller conductivity, while it could be ascertained by determinations of the freezing-point that it had not entirely split up into its components in aqueous solutions.

The discovery of this compound made a renewed investigation of the boro-pyro-catechates necessary.

¹⁾ Recueil 37, 184 (1917).

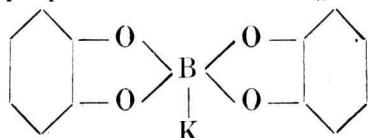
²⁾ Cf. These Proc. following communication.

Mr. HERMANS, who undertook this investigation (c.f. following communication) soon succeeded in clearing up the composition of these compounds.

The empirical formula $\text{KBO}_4(\text{C}_6\text{H}_4)_2$ applies to the beautifully crystallized potassium salt; the volatile ammonium salt is $\text{NH}_4\text{BO}_4(\text{C}_6\text{H}_4)_2$, aniline salt $\text{C}_6\text{H}_5\text{NH}_2\text{HBO}_4(\text{C}_6\text{H}_4)_2$, from which through careful heating in vacuum, the free acid $\text{HBO}_4(\text{C}_6\text{H}_4)_2$, (prepared and analysed by Mr. MEULENHOFF) was obtained.

There are, accordingly, two pyrocatechol rests bound to the boron atom, in which an *entirely new type of compounds originates*, as the potassium salt hardly reacts alkalically, and, as has been known for a long time already, the relatively strong acid nature of the hydrogen derivative manifests itself in aqueous solution by increase of the conductivity.

In view of the empirical constitution and this modification of properties the below-given structural formula naturally suggests



itself, in which we must imagine the anion of a relatively strong acid to have arisen through binding of the fourth oxygen atom to the boron. The acid is partially hydrolysed by water, but can be sublimated undecomposed in anhydrous condition. Also in its spatial structure the anion will be an antipode to the cation of the ammonium compounds; the four O atoms will lie in the four angles of a tetrahedron, and the two benzene rings then are vertical to each other.

The discovery of this type of boron compounds throws light on the composition of a great number of other boron compounds, and indirectly gives a powerful support to the recent considerations on the atomic structure in general. In this connection we must devote a few words to LEWIS¹⁾ and LANGMUIR's²⁾ atomic model, and to the natural system of elements according to KOSSEL³⁾.

Very much simplified and somewhat modified⁴⁾ these hypotheses come to what follows:

The atom is assumed to be a positive nucleus surrounded by different shells of electrons, in which the number of electrons must

¹⁾ G. N. LEWIS. Journ. Am. Ch. Soc. **38** 762 (1916).

²⁾ IRVING LANGMUIR ibid **41** 868 (1919) and **42**, 274 (1920).

³⁾ Ann. der Physik **49** 229 (1916).

⁴⁾ I wish to state here emphatically that I apply these considerations exclusively to the *first* period of the system, because I consider the atoms of the second period already to be too complicated to satisfy the simple postulates.

be equal to the excess of protones of the nucleus. The electrons which can more or less easily be shifted, and can even be removed, are found in the outer shell, and also electrons of other atoms can penetrate into this outer shell.

There is further a general tendency to gather eight electrons in this outer shell, because this represents most likely a very stable condition of equilibrium. We meet with this constellation in the noble gases, which do not possess chemical affinity. Only helium has only two electrons in its outer shell, and evidently forms an exceedingly stable whole with the nucleus.

The mono-valent metals have only one electron in their outer shell, and will easily split this off, in this way getting into the condition of the nulli-valent element, which stands one place lower down as to its rank; the elements of the seventh group, the halogens, have seven electrons in the outer shell, and will have a tendency to add one electron, passing with it into the condition of the nulli-valent element, which is one place higher in rank.

Thus an exceedingly stable substance of the type of Helium-Neon will be formed when Li and F are joined, with this difference that there exists a very strong electric field between these atoms, which is wanting in the noble gases.

KOSSEL has designated this kind of bonds by the name of *heteropolar*, they exist between all metallic elements on one side and the non-metallic ones on the other side. When the electron of the metal has entered the shell of the non-metal, this has obtained for the metal-ion a same value as the seven already present ones, which means that the metal-ion is no longer bound to a definite place in the molecule; it can place itself opposite to each of the electrons present.

When the number of electrons in the outer shell increases, resp. decreases, they no longer get so easily quite outside, resp. the power to absorb foreign electrons has diminished; then ensues an interpenetration of the two shells, in which one electron of each of the atoms joins to a pair in the mutual shell division.

This is the *homöopolar* bond according to KOSSEL, in which the two atoms are bound to a very definite place. The hetero-polar or briefly *polar* bond gives rise to molecules which conduct the electric current e. g. in aqueous solution; the homöo- or *non-polar* bond is met with in substances that do not conduct the electric current.

As a type of the first we may name the alkali-halogenides, as a type of the second the organic compounds, but also water, boron-trichloride etc.

In the polar bond the atoms are thought separated, in the non-polar bond they penetrate into each other at definite places.

There is still a third kind of bond, which comes near to the

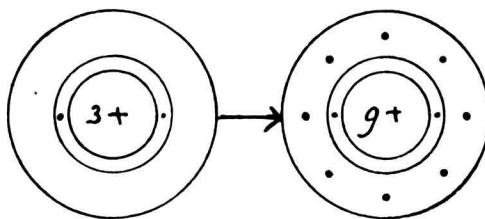


Fig. 1a.
Lithium fluoride.

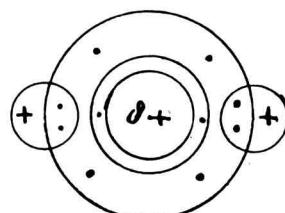


Fig. 1b.
Water.

non-polar bond, and is distinguished from it only in form, not in nature.

It is seen from the symbol for water that the oxygen atom has still two pairs of electrons in the outer shell. These endow this molecule with the power to combine with other molecules, and especially with those of which one of the atoms lacks a few electrons in the outer shell.

Thus we must imagine that metal atoms which have ceded their electrons to acid rests on the salt formation, can get saturated with water molecules, and thus form hydrated metal ions. This kind of non-polar bond is that which was supposed to come about through by-valencies, and which is explained from the tendency to collect eight (or sometimes more) electrons in the outer shell.

It is easy to see that ammonia, though a saturated compound, can combine with a great number of substances owing to the free electrons in the outer shell. All these bonds are of quite the same nature as those that come about through the principal valencies. The penetration of these ammonia molecules into the metal atom often gives it a more pronounced electro-positive character.

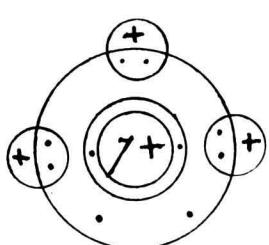


Fig. 2.
Ammonia.

That this bond is really restricted to a definite place of the molecule, follows from MEISENHEIMER's investigation¹⁾, in which he has succeeded in splitting up methyl ethyl aniline oxide into its optical antipodes. The four non-polar bonds, among which that where the nitrogen with its free electrons, has penetrated into the outer shell of the oxygen find a place in the angles of a tetrahedron.

¹⁾ Berichte 41, 3967 (1908).

We point out that the nitrogen here behaves as a tetra-valent substance, the oxygen as a univalent one.

Ammonia, in spite of its having 8 electrons in its outer shell,

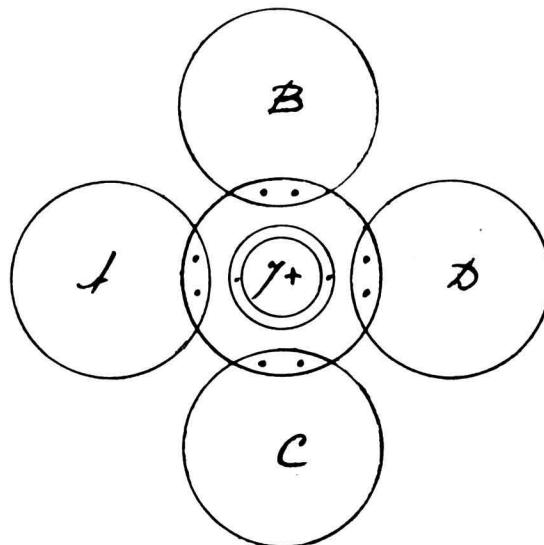


Fig. 3.

$A = \text{phenyl}$, $B = \text{methyl}$, $C = \text{ethyl}$, $D = \text{oxygen}$.

Methyl ethyl phenyl ammonium oxide.

can bind certain definite other atoms non-polarly, provided there be also an atom present that the electron, which is now in excess (and is, therefore, expelled) can take up.

This may also be expressed as follows: ammonia passes into the positive ion condition when forming a bond with a hydrogen atom, or in other words: ammonia can only receive a hydrogen *ion*, as it is saturated with electrons. Here the nitrogen does not become tetra-valent, but penta-valent. This fifth valency, however, has another character: it gives rise to a polar bond.

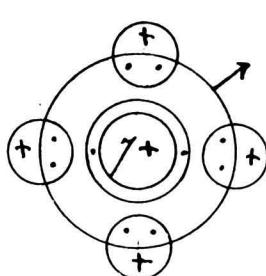


Fig. 4.
Ammoniumion.

We may now apply these considerations to the boron atom, and examine in the first place what is the nature of the bonds in the simple derivatives of this element. The halogen compounds are the most suitable to decide this question.

It is this very power through which a number of atoms, which to start with, have an electro-negative character, acquire the property of an alkali-metal; we need only mention iodine and sulphur.

These have BX_3 as constitution and entirely possess the character of acid chlorides, and not of salts. The three electrons are, accordingly, not ceded, as even the fluorium atoms are non-polarly bound.

In these compounds boron has only six electrons in the outer shell; in some respects they will, therefore, have an unsaturated character (Fig. 5). These halogen compounds can, indeed, become saturated in two ways.

The *first* way, which has been known longest and has already been explained by WERNER to a certain extent, refers to the adoption of a molecule HF. Then there is formed e.g. HBF_4 , a mono-basic acid. It may now be assumed that a fourth atom F becomes non-polarly bound, which, however, is not possible, as boron has no free electron left, unless at the same time an electron (of the H) is taken up, and consequently the group BF_4 passes into the negative ion-condition (Fig. 6).

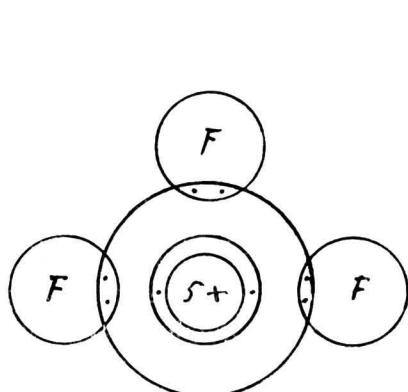


Fig. 5.
Borium fluoride.

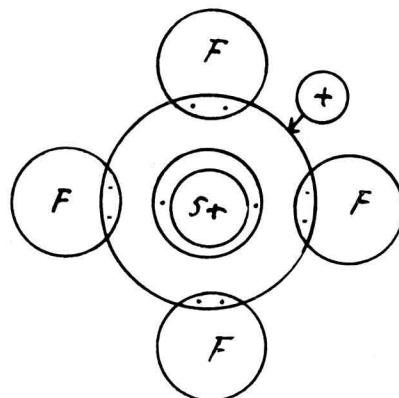


Fig. 6.
Borium fluor hydrogenic acid.

It may also be said that the polarily-bound HF-molecule enters the shell of the boron with two of the electrons of the fluorium atom, the whole BF_4 -group becoming a negative ion.

For the H-ion it is entirely immaterial whether the ceded electron is attached to one of the four fluorium-atoms outside or inside the shell of the boron; as ion it has no fixed place in the molecule, and can wander all round the complex.

In view of the mono-valency of fluorium and of the complex, boron may be assumed to be penta-valent with as much reason as the nitrogen in ammonium compounds.

The *second* way in which boron fluoride can add to its electrons is: to combine with molecules of which there are two electrons

available in the outer shell of one of their atoms, without this giving necessarily rise to ionisation.

Thus BF_3 forms stable compounds with PB_3 and with ammonia,

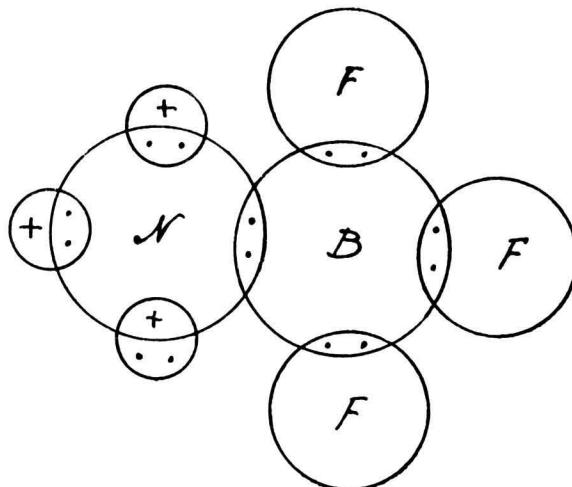


Fig. 7.
Boron fluoride ammonia.

of which the latter can be distilled undecomposed. Their constitution may be represented by the above simplified symbol; the two electrons which the N of the ammonia has in excess have penetrated into the shell of the sphere of the boron, thus forming a non-polar bond. Both atoms have eight electrons in this shell, and are mutually saturated (Fig. 7).

It is not subject to doubt that when different groups are substituted for the H-atoms at the N, a substance is formed which can be split up into its optical antipodes¹⁾.

As regards the valency of the boron, this may be put, like that of the nitrogen, at four, as there is no reason to assume the bond between the N and the B to be of another nature than between the B and the F (resp. between the N and the H).

Let us now proceed to the complex boric acid compounds. The very weak, volatile boric acid itself is, at least for the greater part, a derivative of the tri-valent boron, in which all the bonds are non-polar. In aqueous solution a very small part will be a derivative

¹⁾ It may cursorily be pointed out that the constitution of the addition products of AlCl_3 with a number of organic and inorganic compounds can be seen in entirely the same light.

of the penta-valent boron, in which one of the bonds is polar (see further).

The non-acid complexes agree with this, the acid ones, which are formed with the poly-hydroxy compounds, the hydroxyl groups

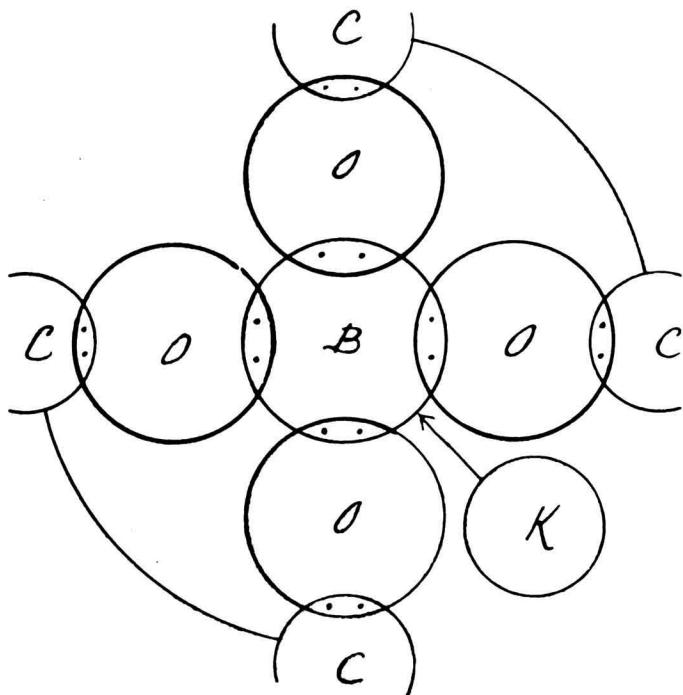


Fig. 9.
Potassium boro pyro catechate.

of which have a favourable position, are derivatives of the penta-valent element. Let us choose as an example potassium boro pyro catechate.

The four oxygen atoms of the two pyro catechol rests are bound to the boron atom. This cannot take place, however, until one electron of a metal or of an H-atom has been ceded to the complex. When this has once been accomplished, it is immaterial for the potassium (or H-) atom, where this electron is to be found in the complex; in view of the tetra-valency of the carbon, of the bi-valency of the oxygen, and of the mono-valency of the complex, the boron may here be assumed as penta-valent; one of these bonds is then polar (Fig. 9).

The four non-polar bonds, just as in the carbon atom — will be grouped as a tetrahedron, so that we may already expect optical activity in mono-derivatives of the pyro-catechol. These complex

boric acid compounds always being more or less hydrolyzed in aqueous solution, the splitting up into optical antipodes will be difficult.

In general the negative ion will be particularly easily formed:

- 1. When the hydroxyl groups of the poly-alcohols have a favourable situation.
- 2. When the organic rests bear an electro-negative character.
- 3. When the other atom easily cedes an electron.

1. The researches on the complex boric acid compounds of the last ten years have proved that the substances with a pronounced acid character from scarcely acid compounds are formed particularly easily, when the hydroxyl groups are situated in one plane with the C-atoms bound to them. It may be assumed that the first phase will be the formation of the derivative of the tri-valent boron. When this complex meets a second molecule of the organic compound, the unsaturateness of the boron will collaborate with the favourable constellation of the poly-alcohol to form the very stable derivative of the penta-valent boron.

2. When this favourable situation of the hydroxyl groups coincides with strongly electro-negative properties of the poly-oxy-compounds, as of α -hydroxy acids and aromatic ortho-hydroxy-acids, these penta-valent boric acid compounds will be exceedingly easily formed. Mr. HERMANS has actually succeeded (cf. following communication) in proving this for boro di-citric acid, and in ascertaining the constitution of the already known boro di-salicylic acid zinc from this point of view.

3. It was to be expected that especially the alkali-salts of these complex acids could be isolated, because the complexes are only realizable on adoption of an electron, and this is easily ceded by an alkali-metal. We meet here with the same influence which the metal atom in general exerts on the stability of the acid rest, which renders it possible to obtain salts of which the corresponding acid is unstable and even unknown.

This latter circumstance renders it also desirable to write the metal atom by the side of the atom to which it has ceded the electron, though in reality the whole complex becomes a charge richer, and it therefore seems indifferent to a certain extent where this metal atom is placed, since as an ion it is not bound to a definite place¹⁾.

¹⁾ That this is not quite immaterial may appear from the different behaviour of AgNO_2 and KNO_2 resp. AgCN and KCN towards alkyl iodides, which will be discussed later.

We are now able to bring some order in the inorganic derivatives of boron.

The volatile boric acid and its esters are, as was stated above, derivatives of tri-valent boron, and as such, somewhat unsaturated. It will try to supply the deficiency by complex formation.

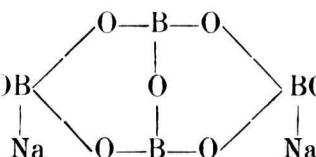
AUERBACH's investigations¹⁾ have brought to light that when an insufficient quantity of a base is distributed between boric acid and arsenic acid there is formed far more borate than was to be expected according to the dissociation constant of boric acid. Complexes must be formed which are much more strongly acid than boric acid in diluted aqueous solution.

Hence in virtue of 3 the added bases cause the quantity of poly-boric acid ion to increase.

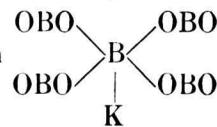
This is corroborated by an investigation of P. MÜLLER²⁾, who could shake out but very little boric acid from a mixture of borate and boric acid with amyl alcohol, though the free acid is easily dissolved in it, evidently because the boric acid was bound with formation of poly-borates in consequence of the above-mentioned kation-action.

These stronger poly-boric acids will be derivatives of penta-valent boron, and accordingly in the symbol a place may be assigned to the metal atoms which promote this phenomenon, next to the boron atom.

The *metaborates* then have the composition $M(BO_3)_n$, *bora*x has the

formula :  while potassium penta borate

KB_5O_8 (see HERMANS, following communication), which crystallizes beautifully from formic acid, possesses the constitution



all assumed to be anhydrous.

There are described a great number of poly-borates; on the condition that the number of penta-valent boron atoms be taken the same as the number of positive metal valencies, their configuration can be easily constructed.

Boric acid anhydride is distinguished from boric acid by its slight

¹⁾ Zeitschr. anorg. Ch. 37 353.

²⁾ ABEGG Handbuch III. 1 p. 32 (1905).

volatility; this furnishes a sufficient ground for assuming this substance to be strongly polymerized. This may possibly be explained from the tendency of the boron atoms of one molecule to form non-polar bonds with pairs of electrons of the oxygen atoms of other molecules. It is possible to form an idea of this polymer by imagining the anhydride molecules to be built up in columns, in which alternately the oxygen atoms have penetrated into the outer shells of the boron atoms, thus contributing to the completion of the "octet". There are enough free atoms left at the oxygen atoms to render the easy hydration to boric acid comprehensible.

The boro hydrogen compounds. From the place of the boron in the system it was to be expected that the affinity of the H should be slight. The interesting investigations by STOCK and his pupils¹⁾ have really proved that these compounds are formed in very small quantities from magnesium boride, and are very unstable. At first B_2H_6 and B_4H_{10} were separated as gaseous boro-hydrogens, and later B_5H_9 , besides higher boro-hydrogens. STOCK is of opinion that the boron must be assumed to be tetra-valent in these compounds.

He, therefore, tried to prepare halogen boron compounds BX_4 , in which he did not succeed, which is, indeed, not astonishing in view of what precedes; such a combination can only be realized when at the same time an electron is added.

The B_2H_6 obtained by him is not necessarily a derivative of tetra-valent boron; the BH_3 , which would have to be formed in virtue of the tri-valency of the boron, is evidently so unstable that two molecules inter-penetrate, in which, however, one of the B-atoms must more or less change into the ion-condition. It is actually immediately adopted by KOH with formation of KBOH, (probably a mixture or combination of KBOH, and $KBOH_2$) and H_2 . Accordingly it is a compound with tri- and penta-valent boron, which through this makes the impression of being a derivative of the tetra-valent element (see the symbol on the following page).

Nor need the second gaseous boro-hydrogen B_4H_{10} possess a tetra-valent boron. In this two BH_3 -groups can be bound to each other, each of them bearing a BH_3 -group, while besides two H-atoms have passed into the kation-condition, and the rest, therefore, forms a bi-valent anion. The B_5H_9 , which is, moreover, the most stable boro-hydrogen²⁾, can certainly, not consist exclusively of tetra-valent boron atoms. If it is assumed that one of the boron atoms is bound

¹⁾ Berichte 54 A 142--158 (1921).

²⁾ Berichte 54 A 155 (1922).

to four BH_2 -groups, which at the same time has taken up an electron with H-nucleus, the relative stability and the fact that this boro-hydrogen dissolves in KOH without residue, evidently with formation of a salt, has been explained in a satisfactory way. Its formula is, therefore, $\text{H}[\text{B}(\text{BH}_2)_4]$ with one penta-valent and four tri-valent boron atoms.

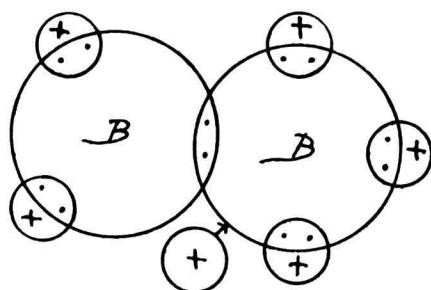


Fig. 10. Borohydrogen.

ion-condition is not possible: $\text{B}(\text{CH}_3)_3$ has been separated, and a polymerisation to $[\text{B}(\text{CH}_3)_3]$, has not been observed — also boro-triphenyl was lately prepared.

That the boro-alkyl compounds can combine with ammonia¹⁾ can be explained in entirely the same way as for BF_3 (cf. p. 103), there is sufficient reason in these non-polarly bound molecules to assume the boron, just as the nitrogen, to be tetra-valent.

Boro-nitrogen. BN. It has not been possible so far to melt, this substance, which forms a white powder and which is very resistant against the action of the air also at high temperature, for which reasons it has been proposed as material for fire proof receptacles; it is very interesting as far as the considerations given here are concerned. In appearance the demand of the valency has been completely fulfilled, as the tri-valent nitrogen is combined with the tri-valent boron. When, however, the properties of nitrogen compounds of other light elements, as cyanogen gas, halogen nitrogen compounds, etc. are considered, boro-nitrogen must at any rate be assumed to be very far polymerized.

When every nitrogen atom is supposed to be surrounded by three boron atoms, and these again each bound to three nitrogen atoms and so on, two electrons of every nitrogen atom remain available in the outer shell for a non-polar bond. Inversely every boron atom can be joined by a pair of electrons. This mutual saturation is here exceedingly probable, because then at the same time an exceptionally stable structure can be attained, viz. that of the carbon in diamond. The properties of boro-nitrogen lead us at any rate to expect

¹⁾ Berichte 54 B 531 (1922). The ammonia compound of boro-trimethyl is a volatile well-crystallizing compound, much more stable when exposed to the air than $\text{B}(\text{CH}_3)_3$ itself.

a very stable configuration. If attempts to bring it to crystallisation should succeed, a substance may be expected with a very high refractivity and very great hardness, and with a still more considerable resistance against external influences than any amorphous product known so far.

The difference with the way of binding of the carbon in diamond is this that one of the bonds at the moment of its formation is not quite equal to the other; when one considers, however, that this difference has vanished after the two elements have combined, so that it is impossible to decide which of the four was this particular bond, the expectation is the more justified that crystallized boro-nitrogen will have the character of diamond.

It is seen that when represented in this way, the idea of the valency begins to diffuse. The boron is more than tri-valent with respect to the nitrogen, because the element lacks something. And the nitrogen is more than tri-valent with regard to the boron, because in the simple compound this element has something too much. Combined they make, therefore, the impression of two tetravalent elements. Hence the valency is replaced by WERNER's coordination value, to which a firmer foundation is given by these considerations.

If it should appear, e. g. from the Röntgenogram, that the diamond structure is applicable to the crystallized boro-nitrogen, this proves at the same time that a distinction between principal- and by-valencies is not rational, and that polar and non-polar bonds should be substituted for this, in which the non-polar bond is a connection between two atoms, which in consequence of mutual repulsion of some such bonds, has taken up a certain place in the molecule, whereas the polar bond forms a connection between one of the atoms and a rest, which will often consist of a multiple of atoms, but which, also when it consists of only one atom, is not fixed to a definite place of it.

It is self-evident that in the first periods, in which the atoms are simply composed, the number of pairs of electrons will not be greater than four, and the coordination-value will not exceed this number.

As the atoms get more complicated, the coordination-value can also increase; we see this already happen in the second period in aluminium, many compounds of which are known, in which this element is bound non-polarly to six atoms.

With regard to the other boron compounds, I will still draw attention to additional compounds of the boric acid esters with

alcoholates, e. g. $\text{Na}[\text{B}(\text{OCH}_3)_4]$, which entirely possess the character of salts in absolutely alcoholic solution — they are decomposed by water.

The boron is non-polarly bound to the four mono-valent OCH_3 -groups, which is only possible through the complex having taken up one electron.

A very interesting group of compounds has been found by W. DILTHEY¹⁾. He found that when acetyl acetone-rests had substituted two chlorine-atoms in BCl_3 , the third chlorine atom assumed the character of an anion, hence the rest of a cation. He rightly calls these substances *boronium compounds*: the considerations developed

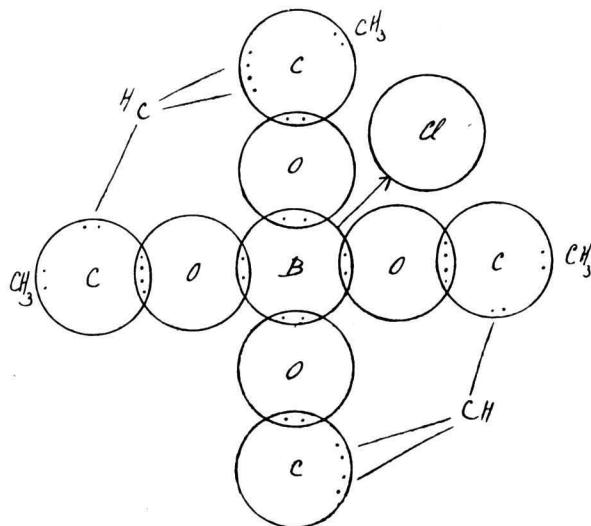


Fig. 11.
Boron di-acetyl acetone chloride.

above account satisfactorily for the phenomenon. The two acetyl acetone rests have as enol replaced two of the chlorine atoms of BCl_3 , and then are bound non-polarly to the boron atom. The favourable situation of the $\text{C}=\text{O}$ -groups with regard to the boron-atom now gives rise to the penetration of two electrons of each of the oxygen atoms into the outer shell of the boron, causing non-polar bonds; this is, however, only possible, when at the same time the third chlorine atom, which was at first non-polarly bound, passes into the (polarly-bound) anion state and the boron complex becomes a cation.

¹⁾ Annalen 483, 300 (1906).

There is certainly no need to state explicitly that only a sketch has been given in the above. It seemed, however, desirable to me to test KOSSEL's and LEWIS-LANGMUIR's hypotheses by the simplest atom that can be bound both polarly and non-polarly to other atoms, for it is to be expected here that the complex compounds will be built up in the least complicated way.

Complications occur in the elements of the second period, e.g. Al, Si, and S, as appears from the existence of compounds as Na_3AlF_6 , K_2SiF_6 and the derivatives of the hexa-valent sulphur. In connection with the above it would have to be assumed that these atoms try to bring together six pairs of electrons in their outer shell, which then possibly might have to be ascribed to the influence of the electrons of the first spherical shell on those of the second. Before this can be examined more closely, the phenomena referring to the simplest elements will first have to be more fully cleared up.

In the case of boron it is, indeed clear, that as regards the formation of compounds *pairs* of electrons play an important part, and that especially the non-polar bond, i.e. the bond that does not conduct electrically, is brought about by such pairs. If it is further borne in mind that the latter kind of bonds is much less reactive than the former, it is natural to suppose that the difference between polar and non-polar bond consists in a greater closeness of the latter. The non-polar bond might be compared to an electro-magnet with a well-closed armature or a toroid, whereas in the polar bond the armature is removed or the toroid opened.

A similar image might be applied to the action of catalysts, in which it is likewise assumed that closed bonds are opened, which gives rise to a greater chance of interaction when meeting other molecules.

Delft, Dec. 1922.
