CCXVIII.—Boron Thiocyanate.

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THE thiocyanates of phosphorus and silicon were first described by Miquel (Ann. Chim. Phys., 1877, [v], 11, 343); they have since been investigated by A. E. Dixon (Trans., 1901, 79, 541) and J. E. Reynolds (*ibid.*, 1906, 89, 397).

The corresponding boron compound was all uded to by Miquel, in the paper mentioned above, as follows: "Finally, after experiments as yet incomplete, I can assert that boron bromide reacts similarly with lead sulphocyanide to give a sulphocyanide with properties analogous to those of the silicon compound."

Boron bromide reacts with silver thiocyanate with the formation of boron thiocyanate, which is extracted from the product by means of cold benzene.

The boron bromide was prepared according to Gattermann's method (*Ber.*, 1889, **22**, 195) by the action of bromine on crude boron, obtained by the action of magnesium powder on anhydrous borax. The final distillation was carried out with care, since the mercuric bromide formed after decolorisation of the crude product with mercury is carried over in appreciable quantities in the last portion of boron bromide vapour.

To prepare the boron thiocyanate, a small bulb of boron bromide was placed together with twice the theoretical quantity of thoroughly dried silver thiocyanate in a well-stoppered bottle, pure benzene added, and the bulb broken by vigorous shaking. The shaking was continued for a few minutes, after which the colourless solution of the thiocyanate was filtered, and the benzene removed at the ordinary temperature by means of a current of dry air. The substance was deposited in glistening, colourless crystals, and a further quantity could be obtained by extracting the residual silver salts with benzene.

Traces of hydrolysis occur unless extreme care is taken, the crystals becoming clouded and discoloured as the solution becomes concentrated. Analysis gave :

B = (i) 5.8, (ii) 6.3, and (iii) 5.8.N = (i) 21.6 and (ii) 22.3. S = (i) 51.6 and (ii) 51.8.

 $B(SCN)_3$ requires B = 5.9; N = 22.7; S = 51.9 per cent.

The substance separates from benzene in short, rhombic crystals, or sometimes in the form of radiating needles. It crystallises from ether in thin, colourless plates.

When heated on a platinum wire in the Bunsen flame, the thiocyanate burns, leaving a charred residue, which, on ignition, gives boron nitride. In the absence of air, it is largely destroyed on heating, only a small portion distilling unchanged.

At 100° the substance darkens considerably, and a benzene solution deposits brown flocks when it is boiled.

When exposed to moisture or treated with alkalis, the thiocyanate is at once hydrolysed to boric and thiocyanic acids, a solution of ferric chloride giving an intense coloration.

With the view of determining whether the substance possesses the constitution of a thiocyanate, $B(SCN)_3$, or of a thiocarbimide, $B(NCS)_3$, its behaviour towards aniline was investigated.

A. E. Dixon has shown (*loc. cit.*) that the corresponding phosphorus compound acts as a thiocarbimide towards the base, yielding the corresponding thiocarbamide, whereas from the work of J. Emerson Reynolds the silicon compound exhibits the behaviour of a thiocyanate.

A solution of the boron compound in benzene was added to a concentrated solution of aniline in the same solvent. Some heat was evolved, and a mass of white crystals was precipitated. These were washed by decantation with benzene, drained, and dried, access of moisture being avoided as much as possible.

The crystals contained no boron, but gave reactions for aniline and a thiocyanate; they melted at about 78°, softening before that temperature was reached. The substance gave no thiocarbamide reactions when freshly prepared, but after boiling with water, or allowing it to stand for some time, a mirror of lead sulphide was obtained on warming a portion with an alkaline solution of lead.

The substance had in fact been converted into phenylthiocarbamide,

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which melts at 154° ; a specimen prepared from the original crystals melted at 153° . On analysis :

0.0914 gave 14.2 c.c. N_2 (moist) at 11° and 756 mm. N = 18.6. 0.4136 ,, 0.6679 BaSO₄. S = 22.2.

 $C_7H_8N_2S$ requires N = 18.4; S = 21.1 per cent.

The above experiments thus indicate that the boron compound in solution behaves as a thiocyanate rather than as a thiocarbimide.

The boron remains in solution in the benzene probably as the anilide of boron, but it was not isolated as such; the anilide, which does not seem to have been described, is extremely soluble in benzene, and can only be obtained from a solution in that solvent by concentrating and keeping the resulting gum for some time.

In conclusion, I wish to express my best thanks to Dr. Baker for the helpful interest he has taken in the above work.

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