

XCIX.—*A New Sulphide of Nitrogen.*

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WHEN the yellow sulphide of nitrogen, N_4S_4 , is heated in a vacuum, it sublimes without decomposition. At 100° the vapour pressure is appreciable, and a sublimate soon makes its appearance when one end of an exhausted glass tube containing a little of the sulphide is heated in a steam-jacket.

In the course of some attempts to effect quantitative analysis of the vapour by means of silver gauze, it was observed that, whilst at temperatures above 200° decomposition was complete, very little action took place when the silver was kept at temperatures of 100 — 120° . Advantage was taken of this fact to remove the last traces of free sulphur from nitrogen sulphide.

Into a vertical glass tube about 1 cm. in diameter, 1—2 grams of powdered nitrogen sulphide were dropped, and a roll of silver gauze was pushed in above so as just to touch the sulphide. The tube was then drawn out 3—4 cm. beyond the top of the gauze, and attached by quill tubing to a mercury pump. After exhaustion in the cold, the vertical tube was heated in a steam-jacket up to the level of the top of the silver. The sulphide slowly volatilised, and the bulk of it deposited as a crystalline crust immediately above the silver. During the experiment the gauze was gradually covered with a film of silver sulphide, and a very small quantity of nitrogen was continuously evolved.

After a few hours' heating, when there was a conspicuous sublimate of the yellow sulphide, a faint blue film was observed lining the quill tubing leading to the pump. This film gradually increased in quantity and in extent in both directions. If the experiment was pushed sufficiently far, the blue deposit crept down the tube until it overlapped the crystals of yellow sulphide, forming an intermediate green zone, while it spread a foot or more along the quill tubing in the direction of the pump. The colour of the deposit increased to a fine, deep blue when viewed by transmitted light, until finally those portions of the tube which were most thickly coated became opaque. By reflected light, the colour was bronze, with a metallic lustre.

It should be noted here that the formation of a blue substance was observed by O. C. M. Davis when heating the compound $N_4S_4, SbCl_5$ in a vacuum, but the quantity obtained was too small to investigate.

When all the yellow sulphide had been sublimed, the tube was

cooled, air was let in, and the portion containing the blue substance was broken off for examination. The film was extremely thin, and yielded an unweighable quantity of bronze-coloured fluff when scraped out with a knife.

The substance was conveniently examined by treating with various reagents small pieces of quill tubing which were coated with the film. It was found to be quite insoluble when boiled with several organic liquids which dissolve the yellow sulphide, such as ether, chloroform, benzene, or carbon disulphide. On shaking or warming a piece of the tubing in water, the film rapidly scaled off, and was slowly decomposed. On adding a few drops of bromine water, solution was accelerated, and the resulting liquid gave a precipitate of barium sulphate when mixed with a solution of a barium salt.

When another portion was warmed with a solution of sodium hydroxide, ammonia was evolved.

When heated in air, the substance was decomposed with the evolution of vapours having an odour somewhat like that of iodine, and recalling that of a foul gun-barrel. This may have been due to the presence of the liquid sulphide of nitrogen, N_2S_5 , described by Muthmann and Clever (*Zeitsch. anorg. Chem.*, 1897, **13**, 200). When heated in a vacuum, the substance showed no signs of volatilising at 100° , and it could be freed in this manner from any accompanying yellow sulphide.

When a small quantity was heated in a melting-point tube, decomposition occurred without liquefaction, the substance turning yellow at about the melting point of the yellow sulphide (188°).

A small tube containing a few specks of the compound was exhausted and sealed up, and then rapidly heated to a temperature a few degrees below the melting point of the yellow sulphide in the vapour of boiling aniline. A blue ring was observed to creep up the tube in the wake of the rising aniline vapour, and when the tube was completely submerged, it was seen to be filled with a yellow vapour, which afterwards deposited as crystals on the cooling walls. On examining these crystals with a lens, two distinct types were seen to be present, one consisting of the small, highly refracting crystals characteristic of a sublimate of yellow sulphide of nitrogen, and the other of brown, feathery needles. There were also some milky patches that were probably sulphur. A little nitrogen was found in the tube when the end was broken under mercury.

Many unsuccessful attempts were made to obtain a quantity of the substance sufficient for analysis. The temperature of the silver was varied between 100° and 130° with apparently little effect.

When a very long column of silver gauze—about 100 cm.—was used, no blue compound at all was formed.

A weighable quantity was finally obtained by accident. Nitrogen sulphide was being sublimed in a vacuum over quartz wool, heated to about 300° ; analysis was by no means complete, and among a variety of products were some large, bronze-coloured crystals, which deposited in the connecting tubing leading to the pump. On examination these crystals proved to be identical with the blue substance already described. They broke with a bronze-coloured fracture, were insoluble in organic solvents, and gave the same odour on warming. A single large crystal, weighing about four milligrams, was selected for analysis. It was weighed in a small quartz bucket on an assay balance, and then introduced into a glass tube closed at one end; a small piece of silver gauze was pushed in above it, and the tube was drawn out and connected with a mercury pump by means of a sealed glass junction. After exhaustion, the silver gauze was heated with a naked flame, and the crystal was "sublimed" over it. The lower end of the gauze was coated with sulphide, and the nitrogen evolved was pumped off and transferred to a small constant-volume point gas-burette, where it was measured. The volume reduced to N.T.P. was 1.034 c.c. Taking the weight of a normal litre of nitrogen as 1.2514 grams, the

Weight of gas obtained	=	0.00129 gram
Weight of the crystal	=	0.00433 ,,
Weight of sulphur (by difference)	=	0.00304 ,,

Then, dividing by the respective atomic weights:

$$\begin{aligned}\text{Nitrogen} &= 129/14.01 = 9.21 \\ \text{Sulphur} &= 304/32.07 = 9.48\end{aligned}$$

showing a deviation of only 3 per cent. from the values required by a compound of the composition $(\text{NS})_x$, a satisfactory agreement in view of the very small quantity of material employed.

The new sulphide therefore contains the same relative proportions of nitrogen and sulphur as the yellow sulphide, and affords an interesting example of inorganic polymerism.

The mode of formation of this blue sulphide of nitrogen by the action of silver on the sulphide, N_4S_4 , is not easy to explain. Although its appearance is always accompanied by evolution of nitrogen and the formation of silver sulphide, any quantitative relationship between these phenomena is difficult to detect, because of the very small extent to which the reaction occurs. The fact that the blue sulphide is deposited beyond the yellow on a cooler part of the tube in spite of the demonstrably higher vapour pressure

of the latter suggests that the new sulphide is formed in situ from a volatile and unstable intermediate compound.

This hypothesis is supported by the following observations. Whenever the blue compound was being prepared, the phosphoric oxide between the reaction tube and the mercury pump acquired a red colour. This occurred even when the reaction tube was separated from the pump by many feet of connecting tubing, indicating the presence of a gas or vapour, which combined with or was decomposed by the phosphoric oxide. The red colour changed to green in the presence of air. The mercury in the pump chamber was also attacked. A U-tube cooled in liquid air and a mercury gauge were then introduced into the system. Besides the usual blue film, small quantities of a brown and a white substance were condensed in the U-tube in different zones. The white substance volatilised as soon as the liquid air was removed, and condensed again when the air was replaced, its vapour pressure being clearly indicated by the fall and rise of mercury in the gauge. When communication was established between the U tube and the pump, with the liquid-air vessel removed, the phosphoric oxide was at once discoloured.

In another experiment the U-tube and its contents, while still cooled in liquid air, were sealed off after every trace of nitrogen had been pumped out. The blue film in the U-tube increased on keeping, and a little nitrogen was apparently formed. On the other hand, there was still something present which was condensible in liquid air after the tube had been kept for several days. It is possible that this was sulphur dioxide derived from the traces of oxygen which silver always contains.

The results of these experiments suggest that the immediate precursor of the blue sulphide of nitrogen is a gas or very volatile liquid at the ordinary temperature; that it contains relatively less sulphur, being formed from the yellow sulphide by partial reduction; and that it decomposes on keeping into the blue sulphide and nitrogen. These suggestions are put forward tentatively, because the amount of substance dealt with was so small that quantitative treatment was impossible.

It is at least probable that the sulphides of nitrogen may prove as numerous as their oxygen analogues.

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