CCIX.—*Co-ordination Compounds of Phosphorus and Antimony Pentachlorides.*

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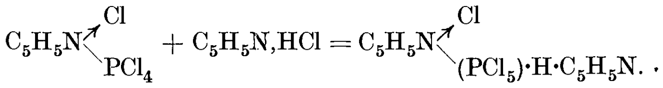
THE tendency of quinquevalent phosphorus to form co-ordination compounds in which the covalency of the element is six is remarkably slight in view of the ease with which the adjacent elements silicon and sulphur form such derivatives. Although compounds of the type $PCl_5,MoCl_4$ and $PCl_5,CrCl_3$ (Cronander, *Bull. Soc. chim.*, 1873, **19**, 501) are known, it is reasonably certain that in these the covalency of phosphorus is four.

The question is of particular interest in that it is not yet certain whether these pentachlorides have an outer shell of more than eight electrons. Holroyd, Chadwick, and Mitchell (J., 1925, **127**, 2492), for example, found evidence for the existence of an ionised form of phosphorus pentachloride, $(PCl_4)Cl$, from conductivity measurements in nitrobenzene solution, and their suggestion receives some support from the results of Plotnikov and Jakubson (*Z. physikal. Chem.*, 1928, **138**, 235) on the conductivity of the pentachloride in bromine. Prideaux (*Chem. and Ind.*, 1923, **42**, 348), on the other hand, maintains the octet theory by assuming that two singlet linkages are present, and this receives support from the numerical value of the parachor for the substance on the assumption that the parachor increment for a semipolar singlet linkage is one half that for a semipolar double linkage.

Although the stability of three of the chlorine linkages apparently differs from that of the other two, the difference is not nearly as great as would be expected from analogy with compounds known to contain a singlet linkage. It is of interest, however, that Kolitowska (*Rocz. Chem.*, 1930, **10**, 743) has found that phosphorus tetrachlorobromide and phenol yield $P(OPh)_3ClBr$, suggesting that one bromine and one chlorine atom differ in the mode of combination from the remaining three chlorine atoms.

The formation of co-ordination compounds of phosphorus pentachloride in which the covalency of phosphorus is six, can be explained on the octet theory only by assuming that two further singlet links are formed, whilst a covalency of seven is not explicable on this basis.

By the action of phosphorus pentachloride on dry pyridine, a co-ordination *compound*, $PCl_6\cdot H\cdot 2C_5H_5N$, has been isolated in the course of the present work; there is evidence that the mechanism of its formation is as follows :



$$C_5H_5N\begin{matrix}\nearrow Cl\\ \searrow PCl_4\end{matrix} + C_5H_5N,HCl = C_5H_5N\begin{matrix}\nearrow Cl\\ \searrow (PCl_5)\cdot H\cdot C_5H_5N.\end{matrix}$$

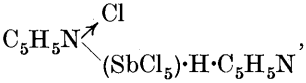
For example, Reitzenstein and Breuning (*J. pr. Chem.*, 1911, **83**, 105) showed that a number of substances containing a negative group formed addition products with pyridine in which the nitrogen atom was quinquevalent, and which yielded with primary and secondary amines a series of red dyes derived from glutaconaldehyde formed by rupture of the pyridine ring. A solution of phosphorus pentachloride in pyridine when warmed with aniline was shown to yield such red dyes, but the above authors were unable to isolate the intermediate addition product. There is presumptive evidence of its formation, however, and the product isolated in the present work is regarded as being a co-ordination compound of this addition compound with pyridine hydrochloride. A valency determination with potassium permanganate, with the usual precautions for the presence of hydrochloric acid, showed the phosphorus to be quinquevalent.

The structure is analogous to that suggested for a similar compound obtained from molybdenum pentachloride and pyridine (Wardlaw and Webb, J., 1930, 2100), *viz.*, $C_5H_5N\begin{matrix}\diagup Cl\\ \diagdown MoCl_3\cdot 2C_5H_5N.\end{matrix}$ A similar derivative of antimony, $SbCl_6\cdot H\cdot 2C_5H_5N$, has been prepared by Weinland and Schmid (*Z. anorg. Chem.*, 1905, **44**, 53) by the addition of an alcoholic solution of pyridine to one of chlorometantimonic acid, $HSbCl_6$. In this case, however, they showed clearly that the compound contained a stable complex, $(SbCl_6)'$, for it was soluble in water and gave with aqueous silver nitrate a yellow silver derivative, $AgSbCl_6,2Py$, and when dissolved in ammonia it gave the corresponding ammonia derivative with ammoniacal silver nitrate. Scarcely any of the chlorine was precipitated by silver nitrate from a solution of the substance in dilute nitric acid. No similar evidence was obtainable for the possible existence of a complex $(PCl_6)'$ in the compound under examination, and it was therefore considered desirable to examine the action of antimony pentachloride on dry pyridine.

With chloroform as a diluent, two *products* were obtained, $SbCl_5,C_5H_5N$ and $2SbCl_5,3C_5H_5N$, the former when an excess of antimony pentachloride was continuously maintained, and the latter when pyridine was similarly in excess. With no diluent, the latter is obtained primarily, but at higher temperatures or on longer standing, a third derivative, $SbCl_6\cdot H\cdot 2C_5H_5N$, can be isolated. This *substance* appears to be different from Weinland and Schmid's compound of similar formula. It is almost insoluble in water and gives with silver nitrate an immediate precipitate of silver chloride, but no yellow silver derivative. It cannot be crystallised unchanged from dry alcohol, and the whole of the chlorine is precipitated in alcoholic solution by alcoholic silver nitrate, and a similar result is obtained when a solution of the substance in aqueous tartaric acid is used. Dissolved in ammonia, however, it gives the yellow silver ammonia derivative with ammoniacal silver nitrate.

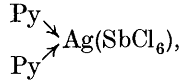
Evidence obtained from antimony derivatives which do not contain the complex $(SbCl_6)'$, with this ammonia reaction, however, showed that the yellow silver compound is probably formed from a decomposition product of the substance in ammonia.

A valency determination by use of potassium iodide showed the antimony to be quinquevalent, and the derivative cannot therefore be represented as a co-ordination compound of antimony tetrachloride and pyridine hydrochloride. It is suggested that the compound has a structure similar to that proposed for the corresponding phosphorus compound, *viz.*,



$C_5H_5N\begin{array}{l}\nearrow Cl\\ \searrow (SbCl_5)\cdot H\cdot C_5H_5N\end{array}$, in which the co-ordination number of antimony is six; and further, that Weinland and Schmid's compound is $SbCl_6\cdot H\cdot C_5H_5N$, containing a molecule of pyridine of crystallisation.

Support for this view was obtained as follows. By treatment of our substance with concentrated hydrochloric acid, a crystalline compound was obtained which appeared to be a mixture of Weinland and Schmid's compound together with a further substance $SbCl_6\cdot H\cdot C_5H_5N$, which was also isolated by them. By fractional crystallisation from alcohol, Weinland's dipyridyl derivative could be separated, and its behaviour in giving a yellow silver derivative with aqueous silver nitrate was confirmed. By continued heating of the mixture with concentrated hydrochloric acid, however, the pure monopyridyl derivative, $SbCl_6\cdot H\cdot C_5H_5N$, was obtained. This substance does not give the yellow silver compound in aqueous solution, but does so in ammoniacal solution, a fact which does not



appear to have been recorded by Weinland. It was found, however, that if pyridine is added to the aqueous solution the yellow silver compound is immediately obtained. This suggests that the silver compound has the structure $\begin{array}{l}\mathrm{Py}\searrow\\ \qquad \mathrm{Ag(SbCl_6)}\\ \mathrm{Py}\nearrow\end{array}$, that of the ammonia compound being similar, and hence they are not formed unless free pyridine or ammonia is present. Weinland's dipyridyl derivative yields this compound in aqueous solution owing to its partial dissociation with the production of pyridine.

In support of this evidence it was shown that all the antimony derivatives obtained in the present work, whether containing the $(SbCl_5)$ or the $(SbCl_6)'$ nucleus, on being warmed with water, gave small quantities of the yellow silver derivative with aqueous silver nitrate when pyridine was added to the solution, while all of them gave the corresponding ammonia derivative when dissolved in ammonia. The quinquevalency of antimony was established experimentally in all the compounds examined.

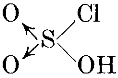
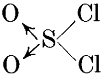
The slow decomposition of the substances by alcohol yielded very complex mixtures on crystallisation. Two substances have been characterised, however, *viz.*, a colourless crystalline compound $2SbCl_5,3HCl,3Py$, which had been prepared by Rosenheim and Stellmann (*Ber.*, 1901, **34**, 3377), and a red crystalline *compound*, $2SbCl_5,2HCl,3Py$. Both these are obtainable by the action of alcohol on the compound $2SbCl_5,3Py$.

Phosphorus thus appears to be capable of exercising a covalency of six, a property which is firmly established in the case of antimony, but hitherto no clearly established example of a covalency of seven in the case of either of these elements appears to have been observed. For example, in derivatives of antimony such as $SbCl_5,MgCl_2,10H_2O$, aqueous silver nitrate precipitates rather more than one atom of chlorine, whereas in the derivative $SbCl_5,2HCl,2C_9H_7N$, alcoholic silver nitrate precipitates $1\frac{1}{2}$ atomic proportions of chlorine (Weinland and Schmid, *Z. anorg. Chem.*, 1905, **44**, 50), indicating that only part of the chlorine forms a complex anion with antimony. The experimental evidence is still inconclusive, therefore, concerning the existence of singlet linkages in the pentachlorides under consideration.

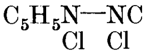
Co-ordination as a Preliminary to Chemical Action.—Sidgwick (Pres. Address, Brit. Assoc., 1927) expressed the view that "chemists have tended to rely too much on supposed modification of linkages within the molecule and have not sufficiently considered the possibility of the formation of co-ordination compounds with the reagents employed." The work carried out by the authors on the pentachlorides of molybdenum, phosphorus, and antimony indicates that Sidgwick's suggestion may be applied with success to chlorination. It has been shown, for example, that molybdenum pentachloride and ether form a co-ordination compound, $MoCl_5,2Et_2O$, which on heating yields ethyl chloride, ether, and derivatives of $MoOCl_3$ (Wardlaw and Webb, J., 1930, 2100). Similarly, it was found in the course of the present work that phosphorus pentachloride has a greater solubility in solvents likely to co-ordinate with it, such as aldehydes, ketones, and esters, than in solvents not containing a "donor" atom. Evaporation of such solutions in a vacuum gives uncrystallisable residues which, on being heated, yield typical chlorination products of the solvent. Liebermann and Landshoff (*Ber.*, 1880, **13**, 169) obtained an addition compound $3PCl_5,2Et_2O$, which was similarly decomposed to ethyl chloride and phosphorus oxychloride. A simple mechanism for this change would be $Et_2O \rightarrow PCl_5 = 2EtCl + O \leftarrow PCl_3$.

It is clear from this that phosphorus oxychloride should contain a semipolar linkage, which is in accord with other experimental evidence. The formation of the ethylphosphoric acids is capable of a similar explanation. Further evidence is available in the case of antimony pentachloride. Williams (*Ber.*, 1876, **9**, 1136) isolated a co-ordination compound $SbCl_5,EtOH$, which on heating yields ethyl chloride and hydrogen chloride, and the corresponding ether derivative $SbCl_5,Et_2O$ behaves similarly. Rosenheim (*Ber.*, 1901, **34**, 3380) showed that antimony pentachloride forms co-ordination compounds with acetaldehyde, benzaldehyde, and acetone. Forster, Cooper, and Yarrow (J., 1917, **111**, 809) isolated a derivative $FeCl_3,Et_2O$ which gave ethyl chloride on heating, and Kuhlmann obtained a similar result with $SnCl_4,Et_2O$. The evidence suggests that the simple mechanism proposed in the case of the chlorination of ether by phosphorus pentachloride may be generally true for the chlorination of compounds such as aldehydes, alcohols, and ketones.

It would be expected that a similar mechanism might be operative in the chlorination of other types of compound capable of co-ordinating with the chlorinating agent, and pyridine affords an instance of this, for all its co-ordination compounds with phosphorus and antimony pentachlorides isolated in the present work yield chloropyridines when warmed with the base itself, as does also the molybdenum compound previously referred to (Wardlaw and Webb, *loc. cit.*). Reitzenstein and Breuning (*loc. cit.*) showed that direct chlorination of pyridine gave an unstable product of the probable composition $C_5H_5NCl_2$ which, in the presence of moisture, yielded the hydrated hydrochloride of dichloropyridine. It is also of interest that antimony pentachloride with solutions of naphthalene or anthracene in carbon tetrachloride gives coloured precipitates of an addition product prior to chlorination (Hilpert and Wolf, *Ber.*, 1913, **46**, 2215).

Sidgwick showed that his hypothesis explained the mechanism of hydrolysis of non-metallic chlorides, and also of acid chlorides of the type R·CO·Cl. Since sulphonyl chlorides containing two semipolar linkages would not be expected to co-ordinate readily, it is noteworthy that the three nitrobenzenesulphonyl chlorides could be crystallised from water, and that, whereas carbonyl chlorides reacted readily with nitrosylsulphuric acid, the corresponding sulphonyl chlorides were inert (Deverall and Webb, J., 1930, 720). Similarly, nitrosylsulphuric acid reacted with the chlorine atom in  but did not attack  (Jones, Price, and Webb, J., 1929, 312). It is considered that Sidgwick's hypothesis is capable of extension to a wide field of chemical reactions.

EXPERIMENTAL.

The Action of Phosphorus Pentachloride on Pyridine.—Sell and Dootson (J., 1898, **73**, 432) stated that phosphorus pentachloride does not react with pyridine at the ordinary temperature, and that even after pyridine has been boiled with a saturated solution of phosphorus pentachloride in phosphorus oxychloride for 14 days, most of the pentachloride can be crystallised unchanged from the solution. These observations appear to be erroneous. On the gradual addition of phosphorus pentachloride to cooled, dry pyridine, crystals of pyridine hydrochloride first separate. Inasmuch as analysis did not distinguish between pyridine hydrochloride and another possible product,  $\underset{\text{Cl}}{C_5H_5N}\text{—}\underset{\text{Cl}}{NC_5H_5}$, the production of the former was confirmed by a molecular-weight determination in chloroform.

Further addition of phosphorus pentachloride causes separation of a colourless crystalline *compound* (Found: P, 7·58; Cl, 53·10; N, 6·70. $PCl_6{\cdot}H{\cdot}2C_5H_5N$ requires P, 7·69; Cl, 52·85; N, 6·95%). The substance is very hygroscopic and is immediately decomposed by water and hydroxylic solvents. It is insoluble in chloroform and benzene, and it should be washed repeatedly with hot chloroform to remove pyridine hydrochloride.

Antimony Pentachloride and Pyridine.—(1) 10 G. of pyridine in 100 c.c. of dry chloroform were added slowly to a cooled solution of 50 g. of antimony pentachloride in 250 c.c. of chloroform, the temperature not being allowed to exceed 25°. The *product* was well washed with hot chloroform and dried in a vacuum (Found:

Sb, 32·10; Cl, 46·72; N, 3·79. $SbCl_5,C_5H_5N$ requires Sb, 31·90; Cl, 47·12; N, 3·79%). The compound forms colourless crystals, decomposed on heating. It is very slightly soluble in water, with decomposition, and is more slowly decomposed by ethyl alcohol, and more rapidly by ammonia. On warming with pyridine, it yields co-ordination compounds of tervalent antimony and pyridine hydrochloride. The antimony in this and the other similar compounds examined was estimated by solution of the substance in concentrated hydrochloric acid and precipitation as sulphide. Alternatively, and in order to determine the valency of the antimony present, the amount of iodine released from potassium iodide was determined with and without the intermediate oxidation of the antimony with potassium chlorate. Chlorine was estimated by solution of the substance in aqueous tartaric acid and subsequent heating for several hours with excess of silver nitrate and concentrated nitric acid.

(2) Conversely, 36 g. of antimony pentachloride in 150 c.c. of chloroform were added slowly to 60 g. of pyridine in 300 c.c. of chloroform, again below 25°. The colourless microcrystalline *product* was well washed with hot chloroform to remove pyridine hydrochloride, and dried in a vacuum (Found: Sb, 28·82; Cl, 43·24; N, 4·93. $2SbCl_5,3C_5H_5N$ requires Sb, 28·88; Cl, 42·65; N, 5·05%).

Unless the pyridine is in considerable excess, mixtures of the above substance and the monopyridyl compound previously described are obtained; these are very difficult to separate, since they are slowly decomposed by alcohol and their solubility in other solvents is very small. Fractional crystallisation from acetone is possible, the monopyridyl compound being less soluble, but the process is tedious and not entirely satisfactory.

By repeated crystallisation of the substance from alcohol two derivatives have been isolated, a red crystalline *compound* (Found: Sb, 26·41; Cl, 46·73; N, 4·60. $2SbCl_5,3C_5H_5N,2HCl$ requires Sb, 26·55; Cl, 46·70; N, 4·66%), and the colourless crystalline product $2SbCl_5,3C_5H_5N,3HCl$, already described by Rosenheim and Stellmann (*loc. cit.*). The red compound is slightly hygroscopic, and all its chlorine is precipitated from alcoholic solution by alcoholic silver nitrate.

On standing, the chloroform solution from the preparation of the original substances deposits further crystalline compounds in which the ratio Sb : Cl = 1 : 6, indicating that chlorination of the pyridine is taking place even in dilute solution.

(3) 50 G. of antimony pentachloride were added slowly to 150 g. of pyridine with cooling after each addition until the separation of a light yellow crystalline compound began. The *product*

was separated by filtration, refluxed with chloroform until free from pyridine hydrochloride, and dried in a vacuum (Found : Sb, 24·40; Cl, 43·10; N, 5·70. $SbCl_6{\cdot}H{\cdot}2C_5H_5N$ requires Sb, 24·42; Cl, 43·28; N, 5·69%). By cooling the reaction mixture in a freezing mixture during the addition of the pyridine, it is possible to isolate the substance $2SbCl_5,3C_5H_5N$ [see (2), above].

The substance now described decomposed when warmed with water, and more slowly with alcohol. If it was warmed with concentrated hydrochloric acid and cooled, small needle-shaped crystals separated which appeared from analysis to consist of an approximately equimolecular mixture of the two substances $SbCl_6{\cdot}H{\cdot}C_5H_5N$ and $SbCl_6{\cdot}H{\cdot}2C_5H_5N$. After prolonged boiling, long, needle-shaped crystals of the former compound separated on cooling (Found : Sb, 29·20; Cl, 51·32; N, 3·41. Calc. for $SbCl_6{\cdot}H{\cdot}C_5H_5N$: Sb, 29·04; Cl, 51·55; N, 3·38%).

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