an einem Quarzkontakt bei 300° C entsprechend der Gleichung

$$3\,P_nH_{n+2} \rightarrow (n+2)\,PH_3 + (2n-2)\,P$$

quantitativ in Phosphor und Phosphin zersetzt wird. Das gebildete Phosphin wird nach Stock u. Mitarb.[4] als Kupferphosphid zur Wägung gebracht. Die Brauchbarkeit des Verfahrens wurde durch Analysen von reinem P_2H_4 und P_2D_4 getestet. Die Methode ist zur analytischen Charakterisierung der Phosphane wesentlich genauer als die Bestimmung des Gesamtphosphors oder -wasserstoffs, deren Prozentgehalte sich bei den einzelnen Homologen nur sehr wenig voneinander unterscheiden, während die Differenzen in dem pyrolytisch gebildeten Phosphin und „Rest-Phosphor" wesentlich größer sind.

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On the Existence of Hexachlorogermanates, $M_2^IGeCl_6$

Germanium tetrachloride is known for its tendency to establish a co-ordination number of six for the germanium by the addition of various other molecules, particularly those containing nitrogen or oxygen with free electron pairs[1]. There is, however, only one recorded example of hexa-coordination achieved by the donation of two more chloride ions to the $GeCl_4$ molecule. This is the compound Cs_2GeCl_6, first prepared by Laubengayer, Billings and Newkirk[2] in 1940. These workers have pointed out that the other alkali and earth alkaline metal ions do not undergo reactions with $GeCl_4$.

In the course of work on the acceptor strength of group IV chlorides for chloride ions in liquid anhydrous HCl[3] we have thoroughly investigated the possibility of the formation of the complex ion, $GeCl_6^{2-}$. Surprisingly, our results indicated the absence of complex ion formation. Germanium tetrachloride is completely insoluble in liquid HCl and does not noticibly increase the self-conductance of HCl, indicating that any equilibrium concentration of $GeCl_6^{2-}$ is immeasurably small. A further proof of the absence of the $GeCl_6^{2-}$ anion, in liquid HCl, is furnished by the distinctly different behaviour of $SnCl_4$ and $GeCl_4$ in this solvent.

When $SnCl_4$ is titrated against the highly conducting solution of 0·2 m tetramethylammonium chloride ($\Lambda = 25{\cdot}0\,\mathrm{cm}^2\,\Omega^{-1}\,\mathrm{mol}^{-1}$) in liquid HCl the conductivity drops sharply until the equivalent point corresponding to a molar ratio of the formula $(Me_4N)_2SnCl_6$ is reached. This compound can be isolated when the HCl is evaporated. On the addition of $GeCl_4$ to the same solution of 0·2 m Me_4NCl in HCl, the conductivity at first slightly increases and then remains constant throughout the titration. When the solution is allowed to warm up, to room temperature in a closed system, the $GeCl_4$ evaporates after the HCl, leaving only the tetramethylammonium hydrogen dichloride, Me_4NHCl_2, as a solid in the cell. Similar results are obtained with tetraethylammoniumchloride.

When nitrosyl chloride is condensed on $GeCl_4$ and then gradually warmed up, $GeCl_4$ and NOCl are miscible in all proportions but no compound formation occurs. Attempts by other workers[4] to prepare $(NO)_2GeCl_6$ have also failed. Laubengayer and co-workers[2] obtained Cs_2GeCl_6 as a flocculent yellowish white precipitate by the addition of $GeCl_4$ to a solution of caesium chloride in a mixture of ethanol and 12 N aqueous hydrochloric acid. Adoption of this technique, using tetramethylammonium chloride, tetraethylammonium chloride, triphenylchlormethane and phosphorous pentachloride as possible chloride ion donors, met with no success. The conditions were then modified systematically and the solvents methanol, ethanol, chloroform, benzene, toluene and nitrobenzene were used, in a variety of mixtures, in the presence and absence of water, and with or without the passage of dry HCl gas. Again no complex salt could be obtained.

Liquid $GeCl_4$ itself did not dissolve any of the chloride ion donors nor did it react with them. Nitrogen containing solvents of a more polar nature such as acetonitrile or pyridine cannot be employed since they form adducts with $GeCl_4$ themselves[5],[6].

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The Preparation of Co-Ordination Compounds of Boron with Halogen Ions as Ligands

In a recent communication[1] concerning the preparation of vinyl- and alkyl dihalogenoboranes the possibility of the existence of complex anions of boron such as $RBX_{3-n}Y_n^-$ has been suggested. This prompts us to communicate the preparation of a number of new co-ordination compounds of boron in which BCl_3 and BF_3 have functioned as acceptors for halogen ions. The following compounds have been obtained.

Table

Compound	Analysis (%)	Description
Me_4NBCl_4	calc.: Cl = 62·5; B = 4·9 found: Cl = 62·5; B = 5·1	A white solid decomposes at 100° C into Me_4NCl and BCl_3
Et_4NBCl_4	calc.: Cl = 50·1; B = 3·8 found: Cl = 49·7; B = 3·8	Similar to Me_4NBCl_4
Me_4NBF_3Cl	calc.: Cl = 20·0; B = 6·1 C = 27·1; H = 7·1; N = 7·9 found: Cl = 17·5; B = 6·1 C = 25·5; H = 6·9; N = 7·6	A white solid, extremely sensitive to moisture
PCl_4BF_3Cl	calc.: Cl = 64·2; B = 3·9 F = 20·7; P = 11·2 found: Cl = 64·7; B = 3·8 F = 19·9; P = 11·3	A white solid, stable to dry air
$NOBF_3Cl$	calc.: Cl = 26·6; B = 8·1 found: Cl = 25·7; B = 7·9	A light yellow solid, with a high dissociation pressure at room temperature
$NO(BEt_3Cl)$	calc.: Cl = 21·7; B = 6.6 found: Cl = 21·0; B = 6·5	M.P. = −36 to −38° C, forming a deep red liquid
PH_4BF_3Cl	calc.: Cl = 25·6; B = 7·8 found: Cl = 22·1; B = 7·7	A slightly yellowish solid, with a high dissociation pressure at room temperature
PH_4BCl_4	calc.: Cl = 75·9; B = 5·8 found: Cl = 73·9; B = 5·8	A fine white powder, behaviour similar to PH_4I
$POCl_3 \cdot BF_3$	calc.: Cl = 48·1; B = 4·9 F = 25·8; P = 14·1 found: Cl = 46·2; B = 5·0 F = 25·2; P = 14·1	A white solid, extremely hygroscopic; M.P. = −3° C with dissociation into BF_3 and $POCl_3$

All the compounds listed in the table, together with others, have been prepared using anhydrous liquid hydrogen chloride as an ionizing solvent. Details of the experimental techniques employed will be given elsewhere[2]. It should be emphasized, however, that all the compounds listed above are extremely sensitive to moisture, and that all manipulations must be carried out in a dry-box. Of these compounds only Me_4NBCl_4, prepared by another method, has been described before[3]. The successful preparation of $NOBF_3Cl$ and of $POCl_3 \cdot BF_3$ provide striking examples of the usefulness of liquid HCl as a media in preparative inorganic chemistry. NOCl and BF_3 are reported to yield the compound $NOF \cdot 2BF_3$ by an unspecified direct interaction[4], and previous attempts to isolate a co-ordination compound of $POCl_3$ and BF_3 had failed[5]). In liquid HCl, however, Cl^- acts quite readily as a donor towards BF_3.

$POCl_3 \cdot BCl_3$[5]) and the already well-known tetrachloroborates $NOBCl_4$[6]) and PCl_4BCl_4[7]) are also easily accessible in liquid HCl. The properties of these compounds obtained in this way were in agreement with those reported in the literature. We have also obtained some evidence for the existence of another addition compound between PCl_5 and BCl_3, of the formula $PCl_5 \cdot 2BCl_3$. This compound very readily loses half its BCl_3 to give PCl_4BCl_4.

The compound $PCl_3 \cdot BCl_3$ was first reported by STIEBER[8]) as a white crystalline solid which could be sublimed without decomposition. We have shown that this compound was in all probability $POCl_3 \cdot BCl_3$. The compound $PCl_3 \cdot BCl_3$ does exist, but it has the low melting point of − 64° C. Any crystalline product retained in the liquid above this temperature is $POCl_3 \cdot BCl_3$ as can easily be proved by comparison of the infrared spectra. Unless very carefully handled PCl_3 is readily oxidised in the presence of air.

Infra-red spectra of the compounds in the table and those mentioned in the text have been recorded. A preliminary analysis of the spectra demonstrates the existence of both the BCl_4^- and BF_3Cl^- anions as distinct structural units. We agree with the view expressed by KYNASTON and TURNER[3]) that the absorption bands in the region 690 and 660 cm^{-1} can be taken as evidence for the presence of the BCl_4^- anion. A detailed analysis of the spectra is in progress and will be published soon.

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Chromium (III) Complexes of Tetra Potassium Molybdenum-octacyanide

A number of metal complexes of tetra potassium molybdenum octacyanide are known. Its complex formation with chromium (III) has, however, escaped the attention of workers in this field. Unlike other metal complexes, the product of the reaction is neither a precipitate nor colloidal in nature. On the other hand on mixing fairly concentrated solutions of the two reactants a slight change in colour takes place which slowly develops into a red one keeping for some time. In order to study this reaction, tetra-potassium molybdenum octacyanide was prepared as described by FIESER[1]) and the strength of its solution determined potentiometrically[2]) against potassium permanganate. Chromic chloride solution was obtained by dissolving green A. R. crystals in doubly distilled water and strength determined iodometrically[3]). The reactants each of concentration 0·02 M were mixed in the ratio, chromic chloride to molybdocyanide as 2:18, 4:16, … 16:4 and 18:2 (the reaction vessels were wrapped with black paper and mixing was carried out in a dark room to avoid the decomposition of molybdocyanide by light). After about two hours appreciable change in colour was observable and this developed into an intense colour after about ten hours.

Complex ion formation was studied photometrically by JOB's method, using Hilger Spekker absorptiometer. Blue filter No. 1 and 0·25 cm cell were used throughout the measurements. The absorption of light was measured at different intervals of time for the mixtures, extending the measurements for a period of 48 hours. The results are given in Fig. 1.

A few absorption studies, using DU Spectrophotometer were also carried out to get evidence for complexion formation. A tungsten lamp as the source of light and 1 cm Corex cell were used throughout the measurements. Optical densities of the various mixtures after keeping them for 48 hours were determined at 470 mμ (wavelength for maximum absorption of the mixture). The values of the optical density in this case, were not the same as found with Hilger absorptiometer. The results with the instrument are given in the table 1.

In spite of the fact that similar values could not be obtained with the two instruments definite evidence for the presence of a complex formed by the inter-action of chromic chloride and tetra potassium molybdenum octacyanide in the ratio 1:1 could be found on plotting the above mentioned values of optical densities against volume of chromic chloride.

Table 1

$CrCl_3$[a])	2	4	6	8	10	12	14	16	18
$K_4Mo(CN)_8$[a])	18	16	14	12	10	8	6	4	2
O. D. I	796	959	1097	1155	1188	1000	745	530	310
O. D. II	13	29	46	63	66	78	86	102	111
O. D. III	552	495	432	1958	1500	1849	190	122	73

a) Vol. of $CrCl_3$ resp. $K_4Mo(CN)_8$ (0.02 M) in cm^3. — O. D. = Optical density × 10^3 of I mixt., II $CrCl_3$, III $K_4Mo(CN)_8$.

Discussion. From the curves in Fig. 1a and 1b it could be seen that there is at least one common ratio (10:10) for $CrCl_3$ to $K_4Mo(CN)_8$ where maximum absorption at different time intervals exists. This clearly shows the formation of the stoichiometic compound $KCrMo(CN)_8$, according to the equation $CrCl_3 + K_4Mo(CN)_8 = KCr\,Mo(CN)_8 + 3\,KCl$. Preliminary work on spectrophotometric studies also point towards the formation of such a compound. Besides this, the nature of the absorption curves changes up to a period of eight hours, maxima existing for the ratio 4:16 (Curves *2*, *3*, and *4*) and also for 14:6 (Curve *3*); readings taken after eleven hours, however, uniformly give the same maximum.

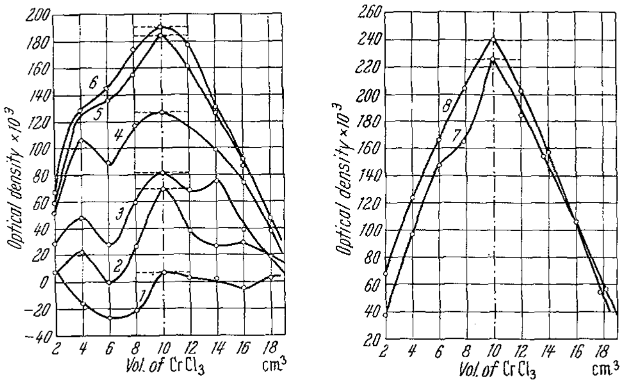

Fig. 1. O. D. of mixture minus sum of O. D. of the components against volume of $CrCl_3$. *1* after 1 hour, *2* after 2, *3* 3, *4* 8, *5* 11, *6* 24, *7* 36, *8* after 48 hrs.

The above mentioned results throw light on the complex nature of the reaction. Firstly, it cannot be purely a stoichiometric reaction since combining ratios like 4:16 and 14:6 are also observed besides the normal ratio of 10:10. Secondly, the development of deep red colour cannot be solely due to complex ion formation but may be due to some changes taking place in the molybdocyanide in presence of chromic ions. In our view the reaction between chromic-chloride and tetra-potassium molybdenum octacyanide at ordinary temperature may be a combined reaction where formation of $KCr\,Mo(CN)_8$ as well as the decomposition (probably hydrolytic) are taking place.

Further work is in progress.

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dl-10-Fluordeserpidin

Unter Anwendung des Prinzips der Reserpin-Totalsynthese von WOODWARD[1]) und der Modifikation von VELLUZ[2])