

THE PREPARATION AND REACTIONS OF SOME
COMPLEXES OF INORGANIC FLUORIDES

A T H E S I S
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A B S T R A C T

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Sulphur tetrafluoride does not form complexes with transition metals in the same way that phosphorus trifluoride does in the compounds $(PF_3)_2PtCl_2$ and $Ni(PF_3)_4$. However, sulphur tetrafluoride does form complexes with metal fluorides and compounds between sulphur tetrafluoride and niobium pentafluoride, tantalum pentafluoride and molybdenum pentafluoride have been prepared.

Sulphur tetrafluoride has been found to be a very useful fluorinating agent for the conversion of mixtures of alkali-metal fluorides and metal oxides, sulphides and carbonyls into complex fluorides. Using this reagent it has been possible to prepare alkali-metal, ammonium, thallous and silver (I) fluoroborates, hexafluorosilicates, hexafluorogermanates, hexafluorostannates, hexafluoroplumbates, hexafluorophosphates, hexafluoroarsenates, hexafluoroantimonates, hexafluorotitanates, hexafluoroniobates, hexafluorotantalates, hexafluoromolybdates (V), hexafluorotungstates (V), and hexafluorouranates (IV).

Adducts of the type $Ph_3CX.BY_3$ (where X or Y = F or Cl) have been prepared. The compounds contain triphenylmethyl

carbonium ions but infra-red and nuclear magnetic resonance spectroscopy are not definite in showing the presence of mixed haloborate ions. Tetrachloroborates and tetrafluoroborates undergo rapid halogen exchange in methylene chloride. Boron trichloride displaces boron trifluoride from trityl tetrafluoroborate to give a product which contains chlorine. Similarly boron trichloride and boron tribromide react with crystalline sodium tetrafluoroborate and a possible mechanism for these reactions has been suggested.

Olefines and acetylenes react with aqueous solutions of sodium hexafluoroplatinate(IV) to induce hydrolysis of the complex fluoro anion. The olefines are oxidised and acetylenes undergo addition of the elements of water to give aldehydes or ketones during the course of the reaction. The hydrogen fluoride produced in the hydrolysis reacts with the olefines to produce mono fluoro alkanes.

Attempts to prepare olefine-metal-fluorides in non-aqueous solvents have been unsuccessful but preliminary reactions of hexafluorobut-2-yne with palladium trifluoride and platinum tetrafluoride give complexes. The trifluoride

polymerises the acetylene to a red oil but insufficient analytical data prevents any type of definite formulation for the other products.

A C K N O W L E D G E M E N T S

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C O N T E N T S

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I N T R O D U C T I O N

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Fluorine is the most electronegative of the elements and also the most reactive. It will combine directly with all the other elements except nitrogen and the rare gases, giving compounds in which the second element frequently exhibits its maximum covalency. Its high reactivity is associated with the low bond dissociation energy which is about 37 k cal/mole.¹ This low value, particularly by comparison with the dissociation energies of the other halogens² has been attributed to the repulsion between the unshared electrons on the bound fluorine atoms³ or to the absence in fluorine of strengthening of the bond by hybridization of the p-⁴ and d-⁵ orbitals which may occur in the higher halogens. A recent explanation of this anomaly has been put forward by Brown⁶ who points out that force constants are generally a good measure of bond strengths and that when these are considered the bond strengths of the halogens appear to fall along the series from fluorine to iodine as expected. Using the force constant as an indication of the high bond strength in fluorine Brown suggests that the observed low bond dissociation energy results from the large energy

required to promote fluorine atoms to the valence state from which the bond may be formed.

Fluorine forms stronger bonds than do the other halogens. Its covalent radius is 0.71Å, compared with 0.99, 1.14 and 1.33Å, for chlorine, bromine and iodine.⁷ The low covalent radius favours greater overlap of the bonding orbitals and this enhances the bond strength. Also if the weak bond in the fluorine molecule is due to repulsion of non-bonding electrons it seems not unreasonable that as the molecule is split into atoms, which then combine with elements to form compounds in which there are few or no unshared electrons on the central atom (e.g., CF_4 , SF_6), such repulsion should disappear.⁸ This then may also be a reason for the "abnormal" strength and shortness of bonds in other compounds formed between elements of widely differing electronegativities (e.g., C and O, P and O, Si and F).

The radius of the fluoride ion (1.36Å) is close to that of the O^{2-} ion (1.40Å⁷) and, as a result, there is often a similarity in the crystal structure of ionic fluorides and oxides of the same type. Thus, for example, NaF and MgO both have a rock salt structure, while PdF_2

and SnO_2 have a rutile structure. The crystal structure of metallic chlorides, bromides and iodides are usually quite different from those of the corresponding fluorides, and resemble those of the sulphides and selenides.⁹ This also stems from a similarity in the ionic radii.

As fluorine tends to bring out highest oxidation states any fluorinating agent which tends to be less powerful than elementary fluorine is always useful in the preparation of lower valency fluorides. In this respect sulphur tetrafluoride is a particularly useful fluorinating agent¹⁰ since the reactants are not always oxidised to the maximum valency state.

Phosphorus trifluoride is in some instances able to replace carbon monoxide as a π -bonding ligand e.g. Wilkinson's $\text{Ni}(\text{PF}_3)_4$.¹¹ Of all the phosphorus trihalides the fluoride forms the most stable complex since the increased electronegativity of the ligand facilitates the removal of electron density from the nickel. No sulphur tetrafluoride complexes analogous to phosphorus trifluoride complexes are known at the present time but in common with selenium tetrafluoride, iodine pentafluoride and bromine trifluoride, sulphur tetrafluoride forms complexes of

unknown structure with metal fluorides.¹²

There are relatively few complexes known in which fluorine and a π -bonding ligand are joined to the same transition-metal atom. This type of complex is well known with the other halides (e.g.s, Zeise's salt, carbonyl metal chlorides, bromides and iodides) and in these compounds there is the possibility of additional back bonding by the halogen. This effect is unlikely to be repeated in the corresponding fluorides which may have different stoichiometry and properties from the compounds formed by other halogens. Thus the known carbonyl metal fluorides have been formulated as $[\text{Rh}(\text{CO})_2\text{F}_3]_2$ and $\text{PtF}_9(\text{CO})_2$.^{13,14,15} The rhodium compound is regarded as a normal carbonyl halide with bridging through the fluorine atoms. However, in the platinum compound the carbonyl stretching frequency is higher than in free carbon monoxide and it is considered that in view of the high oxidation state and electronegative character of the fluorine atoms there is a minimum of π -bond interaction between the carbonyl group and the metal. Other π -bonding ligands such as triphenylphosphine form complexes with metal fluorides and the complexes $\text{Ph}_3\text{P.WF}_6$ ¹⁶ and

$(\text{Ph}_3\text{P})_2\text{PtF}_2^{14}$ have been reported. However, no olefine-metal-fluorides are known at present.

The F^{19} nucleus occupies an important position in nuclear magnetic resonance spectroscopy. The fluorine nucleus like the proton has a spin of one half and substitution of fluorine for hydrogen in a compound often yields nuclear magnetic resonance spectra which are very similar in appearance to the corresponding proton spectra. Like the proton, the F^{19} nucleus gives rise to strong resonance signals. It has a definite advantage over the proton in that the range of chemical shifts of F^{19} in fluorine compounds is about an order of magnitude larger than the corresponding shifts in hydrogen containing compounds. Accordingly the instrumental requirements for high resolution to obtain information comparable with proton measurements are usually not as demanding. In the present work nuclear magnetic resonance has been used to study mixed haloborate anions.

During and since World War II, when the production of fluorine was stimulated by the demands of the Nuclear Programme, there has been a considerable effort devoted towards the study of organic and inorganic fluorine compounds.

Hydrofluoric acid has become a very important commodity in the chemical world. It is a key source material in the production of inorganic fluorides and fluorocarbons and the latter materials are used as refrigerants, aerosols, plastics, dielectrics, lubricants, coolants, fire extinguishers, solvents, heat transfer agents, pharmaceuticals and for many other purposes. Fluorine chemistry has reached an exciting stage and shows great promise for the future.

CHAPTER I

SULPHUR TETRAFLUORIDE COMPLEXES

According to current views of the nature of the co-ordinate link between donor ligands and transition metal atoms or ions the ability of the ligand to participate in metal ligand π -bonding is often essential to the overall stability of the metal ligand bonding. Presumably it is always necessary that the ligand has some ability to form a σ -donor bond, but in many cases the π -bond seems to be by far the more important. Thus in phosphorus trifluoride the phosphorus atom can form $d\pi-d\pi$ -bonds with metals by using its unfilled $3d_{xy}$ and $3d_{yz}$ orbitals. It appears that while the three highly electronegative fluorine atoms greatly reduce the donor power of the phosphorus atoms as is evident by the inability of phosphorus trifluoride to form complexes with even strong but simple acceptors such as boron trifluoride,¹⁷ they also markedly increase the stability of the $d\pi-d\pi$ dative bonds.¹⁶ A number of phosphorus trifluoride complexes of metals have been prepared (see Table I) but only a few have been characterised in any detail.

Table I.PF₃ derivatives of metals.

Compound	Remarks
Ni(PF ₃) ₄ ^a	liquid, b.p. 71°
(PF ₃) ₂ PtCl ₂ ^b	solid, m.p. 102°
[(PF ₃) ₂ PtCl ₂] ^b	dec. 285°
Haemoglobin-PF ₃ ^c	complex not isolated
(PF ₃)IrF ₂ ^d	
(PF ₃)OsF ₂ ^d	
(PF ₃)PdF ₂ ^d	
(PF ₃)PtF ₂ ^e	made from PF ₃ plus Pt
(PF ₃)CoF ^d	
(PF ₃) _n RuO ₄ ^f	n = 1, or 2
(PF ₃) _n OsO ₄ ^f	n = 1, or 2

^a Wilkinson, J. Amer. Chem. Soc., 1951, 73, 5501;

^b Chatt, Nature, 1950, 165, 637; ^c Wilkinson, Nature, 1951, 168, 514; ^d Hair and Robinson, unpublished communication quoted by Peacock, Progress. Inorg. Chem., 1960, 2, 193; ^e Moissan, Bull. Soc. chim. France, 1891, 484; ^f Hair and Robinson, J., 1958, 106.

Obviously all the compounds mentioned in this table owe their stability to dative π -bonding.

Now in sulphur tetrafluoride the $3d_{xy}$ and $3d_{yz}$ orbitals are again available for π -bonding just as in phosphorus trifluoride. Moreover, the presence of an additional fluorine atom in sulphur tetrafluoride might be expected to further enhance the ability of the sulphur tetrafluoride to participate in dative $d\pi-d\pi$ -bonding.

Phosphorus trifluoride forms very stable adducts with platinous chloride¹⁹ but all attempts in this work have been unsuccessful in obtaining any reaction between sulphur tetrafluoride and platinous chloride at temperatures ranging from 20 to 300°. These results have also been confirmed by Bartlett and Robinson^{20,21} who found that there was no interaction between platinous chloride and sulphur tetrafluoride or selenium tetrafluoride from -40° to 220°.

Similarly reaction of sulphur tetrafluoride with nickel carbonyl and molybdenum carbonyl in benzene failed to give a zero valent complex analogous to phosphorus trifluoride complexes. The products of these reactions were dark solids whose infrared spectrum showed that all the carbon monoxide had been expelled from the carbonyl and

that they contained no sulphur tetrafluoride. With nickel carbonyl and sulphur tetrafluoride a yellow compound was obtained at -80° but the compound decomposed even at this temperature in about fifteen minutes.

From these reactions it appears that sulphur tetrafluoride will not function towards transition metals in the same way as phosphorus trifluoride. Differences in the reactivity of phosphorus trifluoride and sulphur tetrafluoride can be judged from the following two examples. Phosphorus trifluoride does not react with boron trifluoride¹⁷ whereas there is an immediate reaction between sulphur tetrafluoride and boron trifluoride when the gases are allowed to mix to give the adduct $\text{BF}_3 \cdot \text{SF}_4$.²⁰ The second difference between the two compounds is seen in their reactivity with iridium hexafluoride. The action of phosphorus trifluoride on iridium hexafluoride results in the formation of the compound $(\text{PF}_3)\text{IrF}_2$.²² However, with sulphur tetrafluoride iridium hexafluoride gives the adduct $\text{IrF}_5 \cdot \text{SF}_4$ which on heating in vacuum at $125-130^{\circ}$ loses some sulphur tetrafluoride to give an oil which still contains sulphur tetrafluoride.²³ As $\text{IrF}_5 \cdot \text{SeF}_4$ decomposes under

vacuum at 130° to give $(\text{IrF}_6)_2\text{SeF}_6$ an analogous compound $(\text{IrF}_6)_2\text{SF}_6$ may have been formed.

The only complexes of sulphur tetrafluoride known at the present time are the adducts it forms with a number of inorganic fluorides and these will be considered under the following heading.

Sulphur Tetrafluoride Complexes of Inorganic Fluorides.

The first examples of sulphur tetrafluoride adducts; $\text{BF}_3 \cdot \text{SF}_4$, $\text{AsF}_3 \cdot \text{SF}_4$ and $\text{SbF}_3 \cdot \text{SF}_4$ written in ascending order of stability were first discovered by Bartlett and Robinson²⁰ who suggested they were simple acid-base complexes, e.g. $\text{F}_3\text{B} \leftarrow \text{:SF}_4$. However, this formulation was criticised by Cotton and George¹² who pointed out that sulphur tetrafluoride would be a poorer electron donor than phosphorus trifluoride (which does not interact with boron trifluoride¹⁷) because the extra fluorine atom would tend to make the lone pair less available for interaction with another molecule. Also the F^{19} nuclear magnetic resonance spectrum¹⁰ of the $\text{AsF}_3 \cdot \text{SF}_4$ system down to -60° shows only one type of fluorine environment due to rapid fluorine atom exchange. Association and dissociation of a simple acid-base adduct would not provide a mechanism

for exchange of fluorine atoms bonded to arsenic and of those bonded to sulphur.

The adducts may be salts based on the cation SF_3^+ and this formulation is preferred by Cotton and George.¹⁸ More evidence for this ionic structure is given by Seel and Detmer²⁵ who have obtained an infrared spectrum of a thin film of $\text{SF}_4 \cdot \text{BF}_3$ on a rock salt plate. This shows a strong band at 1050 cm^{-1} which is typical of BF_4^- and a doublet at 908 and 940 cm^{-1} which by comparison with the infrared spectrum of the isoelectronic PF_3 molecule is assigned to the SF_3^+ cation. However, it should be noted that the band at 1050 cm^{-1} could have arisen from interaction of the compound with the sodium chloride plate or by hydrolysis of the adduct which is extremely hygroscopic.

This ionic formulation is consistent with the observation that all the fluorides that form adducts are strong fluoride ion acceptors and form stable fluoro anions e.g. PF_6^- , SbF_6^- and GeF_6^{2-} (see Table II). However, mixtures of sulphur tetrafluoride with silicon tetrafluoride or iodine pentafluoride¹⁰ show no evidence of complex formation or fast fluorine exchange within the

Table II.SF₄ adducts of Inorganic Fluorides.

Adduct	Remarks
BF ₃ ·SF ₄ ^a	sublimes at 80° (atm. pressure)
GeF ₄ ·2SF ₄ ^b	
SnF ₄ ·2SF ₄ ^b	isolated as SnF ₄ ·2HCONMe ₂
PF ₅ ·xSF ₄ ^b	no solid complex isolated but interaction
AsF ₃ ·xSF ₄ ^b	" " " " "
AsF ₅ ·SF ₄ ^a	sublimes at 190°
SbF ₅ ·SF ₄ ^a	m.p. 245° (dec.)
TiF ₄ ·2SF ₄ ^b	isolated as TiF ₄ ·2HCONMe ₂
NbF ₅ ·0.54SF ₄ ^c	
TaF ₅ ·0.39SF ₄ ^c	
MoF ₆ ·0.69SF ₄ ^c	
MoF ₆ ·xSF ₄ ^d	yellow solid at -40°
RuF ₆ ·SF ₄ ^d	dec. at 150°
IrF ₆ ·SF ₄ ^c	m.p. 120-125° (dec.)

^a Bartlett and Robinson, Chem. and Ind., 1956, 1351;

^b Oppegard, Smith, Muetterties and Englehardt, J. Amer. Chem. Soc., 1960, 82, 3835; ^c Present work;

^d Bartlett and Robinson, J., 1961, 3417; ^e Robinson and Westland, J., 1956, 4481.

temperature range -90 to 100° . Since the fluorosilicate anion is very stable it is difficult to explain the lack of interaction here. Similarly iodine pentafluoride readily adds fluoride ion to form IF_6^- .

Muetterties et al.¹⁰ who have drawn attention to the above facts have described another interaction which is fully consistent with the experimental observations. They prefer an association based on fluorine bridge bonds to give a dimeric polymer structure (Diag. I). This type

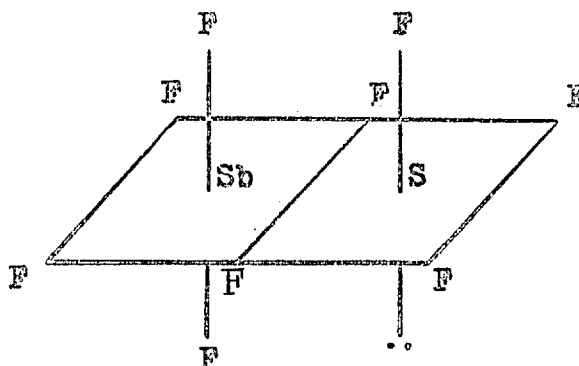


Diagram I.

of interaction is found in HF ,²⁶ SbF_5 ,^{27,28} and $2\text{AsF}_5 \cdot 3\text{SO}_3$ ²⁹ and has been postulated as a fluorine exchange intermediate in SeF_4 , SF_4 ,³⁰ ClF_3 , IF_5 ³¹ and SbF_5 .^{27,28} Most of the fluorides that do interact with sulphur tetrafluoride are not symmetrical molecules and

in forming a fluorine bridge complex these fluorides obtain a higher symmetry and sulphur tetrafluoride would obtain a pseudo octahedral symmetry. The bridged structure has been criticised²¹ on the basis that sulphur tetrafluoride does not combine with caesium fluoride or nitryl fluoride²² to form the SF_6^- ion which would presumably have octahedral symmetry. Thus the tendency for the sulphur atom to attain a pseudo octahedral co-ordination such as it would have in the bridged structure must be small and the pseudo tetrahedral co-ordination of the SF_6^+ ion may be preferred.

Possibly fluorine bridging may be more important in the selenium tetrafluoride derivatives since this tetrafluoride can act as a fluoride ion acceptor to form the SeF_6^- ion²³ in which the selenium is presumed to attain a pseudo octahedral co-ordination.

Bartlett and Robinson²¹ have taken the X-ray powder photographs of some selenium tetrafluoride and sulphur tetrafluoride adducts. The photographs of the sulphur tetrafluoride derivatives are simpler than those of the selenium derivatives but so far the only adduct to be indexed is the compound $\text{SbF}_5 \cdot \text{SF}_6$ which is cubic

($a = 5.625 \pm 0.002$): There is one molecule in the unit cell and although a complete structure determination has not been done the symmetry is suggestive of a SF_3^+ cation. It has already been mentioned that sulphur tetrafluoride has all the requirements to form dative $\text{d}\pi\text{-d}\pi$ -bonds with transition metals. Thus sulphur tetrafluoride adducts of transition metal fluorides could be regarded as complexes in which the sulphur tetrafluoride is acting as a π -bonding ligand.¹⁴ Likewise selenium tetrafluoride and bromine trifluoride adducts of transition metal fluorides could also be regarded as π -bonded complexes.

It is pertinent to remark at the end of this discussion that the structures of these complexes is still unknown. Neither the ionic or bridged structure seem to fit all the data and the final answer will have to wait until a complete X-ray determination has been performed on several compounds.

Sulphur tetrafluoride adducts of niobium, tantalum and molybdenum fluorides.

In the present work previously unreported adducts of sulphur tetrafluoride with niobium, tantalum and molybdenum pentafluorides have been prepared. The adducts were

prepared by fluorination of niobium pentoxide, tantalum pentoxide and molybdenum carbonyl with excess sulphur tetrafluoride in a stainless steel bomb. The stoichiometries of the adducts do not correspond to a 1:1 ratio between the Lewis acid and the Lewis base. The niobium and tantalum compounds analyse as $\text{NbF}_5 \cdot 0.5\text{SF}_4$ and $\text{TaF}_5 \cdot 0.4\text{SF}_4$. When the adduct $\text{IrF}_5 \cdot \text{SeF}_4$ is heated at 125° it loses selenium tetrafluoride and the compound $(\text{IrF}_5)_2 \cdot \text{SeF}_4$ is formed. As the reactions of niobium and tantalum pentoxide were carried out at 350° , by analogy with the decomposition of the compound $\text{IrF}_5 \cdot \text{SeF}_4$,²⁴ the niobium and tantalum compounds could be formulated as $(\text{NbF}_5)_2 \cdot \text{SF}_4$ and $(\text{TaF}_5)_2 \cdot \text{SF}_4$. The molybdenum pentafluoride adduct was prepared at 165° and analysed as $\text{MoF}_5 \cdot 0.7\text{SF}_4$. Presumably dissociation was incomplete at this temperature and the product could have been a mixture of $\text{MoF}_5 \cdot \text{SF}_4$ and $(\text{MoF}_5)_2 \cdot \text{SF}_4$. The complex $\text{MoF}_5 \cdot \text{SF}_4$ was prepared by the reaction of molybdenum carbonyl with sulphur tetrafluoride at room temperature. The adduct was formulated as a pentavalent derivative of molybdenum as fluorination of alkali-metal fluorides and molybdenum carbonyl with sulphur tetrafluoride gave only pentavalent complexes (see Chapter II).

Reaction of sulphur tetrafluoride with tetra-n-butyl tin.

A preliminary reaction of sulphur tetrafluoride with tetra-n-butyl tin at room temperature has shown that one of the products is tri-n-butyl tin fluoride. The other product was presumably n-butyl sulphur trifluoride but this was not characterised. The driving force of the reaction is the high stability of the tri-n-butyl tin fluoride and this reaction should prove to be one of a whole series of reactions in which a metal or non-metal fluoride can be alkylated. Preliminary reactions⁸⁴ have shown this to be true, thus boron trifluoride reacts with tetraphenyl tin to give $C_6H_5BF_2$.

EXPERIMENTAL

Preparation of platinous chloride.

Platinous chloride was prepared by reduction of hexachloroplatinic acid with hydrazine dihydrochloride.³⁵

Preparation of sulphur tetrafluoride.

Sulphur tetrafluoride was used directly from cylinders of the gas which were kindly supplied by E. I. du Pont and de Nemours and Co. Inc. and Imperial Chemical Industries Ltd. Sulphur tetrafluoride was also prepared from sodium fluoride and sulphur dichloride in refluxing acetonitrile³⁶ and was stored in a cylinder. In each experiment the sulphur tetrafluoride was redistilled before use.

Metal carbonyls. Nickel and molybdenum carbonyls were kindly supplied by Professor G. Wilkinson.

Reaction of sulphur tetrafluoride with platinous chloride.

Sulphur tetrafluoride was passed over platinous chloride at 20° and the temperature of the reaction was gradually raised over a period of one hour to 250°. No reaction occurred between these temperatures and sulphur tetrafluoride also failed to react with platinous chloride in a stainless steel bomb at 350°. It was concluded from these reactions that sulphur tetrafluoride

does not react with platinous chloride.

Reaction of sulphur tetrafluoride with nickel carbonyl.

Sulphur tetrafluoride was condensed on to a solution of nickel carbonyl in sodium dried toluene. The reactants were allowed to warm to -80° in an acetone-dry ice bath when a yellow compound was formed. While the excess reactants were removed under vacuum at -80° , the yellow compound gradually turned brown and finally black. A similar decomposition was observed when the reactants were kept at -80° for periods greater than about 15 minutes. An infrared spectrum of the black solid in the sodium chloride region was completely blank and it appeared to be metallic nickel.

Reaction of sulphur tetrafluoride with molybdenum carbonyl.

Sulphur tetrafluoride was passed through a solution of molybdenum carbonyl in sodium dried benzene. There was an immediate evolution of gas presumed to be carbon monoxide and the solution became green in colour. Removal of the solvent under vacuum gave green and black solids. An infrared spectrum of these solids showed that they contained no carbonyl groups.

Reaction of sulphur tetrafluoride with molybdenum carbonyl (resublimed) in a stainless steel bomb at 165°

overnight gave a yellow-brown solid. The compound was extremely moisture sensitive and appeared to be a sulphur tetrafluoride adduct of a molybdenum fluoride. As mixtures of alkali-metal fluorides and molybdenum carbonyl give pentavalent complexes with sulphur tetrafluoride the compound was formulated as $\text{MoF}_5 \cdot 0.69\text{SF}_4$. Found: Mo, 36.1; $\text{MoF}_5 \cdot 0.69\text{SF}_4$ requires Mo, 36.1%. When a mixture of sulphur tetrafluoride and resublimed molybdenum carbonyl was left for five days in a stainless steel bomb the product obtained was a sulphur tetrafluoride adduct of molybdenum pentafluoride. Found: Mo, 34.1; $\text{MoF}_5 \cdot \text{SF}_4$ requires Mo, 32.1%.

Reaction of sulphur tetrafluoride with niobium pentoxide.

A mixture of sulphur tetrafluoride and niobium pentoxide which had previously been dried for three hours at 150° , was heated in a stainless steel bomb overnight at 350° . The white product which was vigorously hydrolysed by water to give a colourless solution was a sulphur tetrafluoride adduct of niobium pentafluoride. Found: Nb, 37.8; $\text{NbF}_5 \cdot 0.54\text{SF}_4$ requires Nb, 37.8%.

Reaction of sulphur tetrafluoride with tantalum pentoxide.

Sulphur tetrafluoride and tantalum pentoxide (dried at 150°

for 2 hours) were heated overnight in a stainless steel bomb at 350° . The white solid which was vigorously hydrolysed by water to give a colourless solution was a sulphur tetrafluoride adduct of tantalum pentafluoride. Found: Ta, 56.8; $TaF_5 \cdot 0.39SF_4$ requires Ta, 56.8%.

Reaction of sulphur tetrafluoride with tetra-n-butyl tin.

A mixture of sulphur tetrafluoride and tetra-n-butyl tin was sealed in a dry Carius tube. At room temperature a white precipitate began to form slowly and overnight the contents of the tube became solid. Excess sulphur tetrafluoride was pumped off of the sticky brown solid and the residue was extracted with hot methanol and filtered. On cooling, white crystals separated out which were recrystallised from hot methanol and dried under vacuum. The product was $(C_4H_9)_3SnF$. Found: C, 46.5; H, 9.2. $C_{12}H_{27}SnF$ requires C, 46.6%; H, 8.8%.

CHAPTER II

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THE PREPARATION OF COMPLEX FLUORIDES BY USE OF SULPHUR TETRAFLUORIDE AS FLUORINATING AGENT.

Complex fluorides have been known to exist for many years and a number of methods are available for their preparation. The first complexes to be isolated were those obtained from aqueous solution and many of these interfered in analytical work e.g. estimation of phosphate in the presence of fluoride ion. Complex fluorides which are insoluble or are not hydrolysed by water are easily prepared in this manner using aqueous hydrofluoric acid. Some complexes can be crystallised from aqueous hydrofluoric acid solution as hydrates e.g. $K_2TiF_6 \cdot 10H_2O$ and can be dehydrated either by warming or if decomposition occurs by heating in a stream of gaseous hydrogen fluoride. However, with the availability of fluorine gas and anhydrous hydrogen fluoride it is generally much easier to use a dry method for the preparation of complex fluorides.

In the present work a new method for the preparation of complex fluorides by the use of sulphur tetrafluoride has been developed. However, before this is described in

detail a brief account of the other more important methods of preparation (some of which have been used in this work) will be given to point out the limitations and advantages of the particular method.

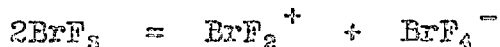
The use of elemental fluorine.

This method of preparing complex fluorides by fluorination of mixtures of metal halides at 200-400° has been largely developed by Klemm and his co-workers.³⁷ The reactions are easily performed in nickel boats contained in nickel tubes and is the most powerful method of all giving high valency metal fluorides. Thus fluorinations of a mixture of 2 parts potassium chloride and 1 part nickel chloride gives K_2NiF_6 ³⁷ while fluorination of a 1:1 mixture of potassium chloride and silver nitrate yields $KAgF_4$.³⁸ Silver(I), thallos and ammonium salts cannot be prepared with elemental fluorine as oxidation of the cation occurs, but the preparation of alkali-metal, magnesium, calcium, strontium and barium salts is possible.³⁹

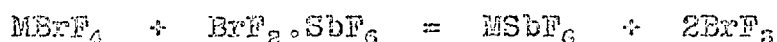
The use of bromine trifluoride.

Besides being a very powerful fluorinating agent bromine trifluoride is a good solvent for metal fluorides.

The liquid is a good conductor of electricity ($K = 8 \times 10^{-3} \text{ ohm}^{-1} \text{ cm.}^{-1}$ at 25°) and the following mechanism is postulated for the self ionisation.⁴⁰



Alkali-metal, silver, strontium and barium fluorides dissolve to give the bases MBrF_4 while acid fluorides such as antimony pentafluoride give the acids $\text{BrF}_2 \cdot \text{SbF}_5$. In bromine trifluoride the acids and bases react giving a complex fluoride according to the equation.



The complex fluorides are easily prepared in silica apparatus and excess bromine trifluoride can be removed under vacuum. Salts prepared by this method are not always pure.^{41, 42} Solvolysis occurs and there is incomplete reaction between acid and base and bromine trifluoride is firmly bound to the compound. Thus pure K_2TiF_6 dissolves in bromine trifluoride and after removal of solvent yields a product $\text{K}_2\text{TiF}_6 \cdot 1.1\text{BrF}_3$.⁴¹

Alkali-metal, silver, barium⁴³ and strontium⁴⁴ salts can be prepared with bromine trifluoride but thallous, ammonium, magnesium and calcium salts are not obtainable.

The use of iodine pentafluoride.

The preparation of complex fluorides using iodine pentafluoride, which is a mild fluorinating agent, has not been studied in great detail. It converts a mixture of potassium fluoride and tungsten carbonyl into the complexes K_2WF_6 and K_3WF_6 the nature of the product depending on the amounts of the reactants used.⁴⁵

Alkali-metal iodide-molybdenum carbonyl mixtures are converted into hexafluoromolybdates(V)⁴⁶ by iodine pentafluoride and potassium fluoride in iodine pentafluoride reacts with tungsten hexafluoride to give K_2WF_6 .⁴⁵

The use of selenium tetrafluoride.

The fluorinating action of selenium tetrafluoride has been little studied although it is reported that an equimolar mixture of potassium fluoride and tungsten trioxide gives a complex $KWOF_6$.⁴⁷

Selenium tetrafluoride has been used as a solvent for the preparation of complex fluorides. Alkali-metal, silver, thallous, ammonium and barium fluorides are soluble in selenium tetrafluoride giving the compounds $MSeF_6$ ⁵³ and a mixture of thallous fluoride and ruthenium

pentafluoride in selenium tetrafluoride gives the complex TlRuF_6 .²⁴ As with bromine trifluoride solvolysis occurs in preparations with selenium tetrafluoride and pure products are difficult to obtain.⁴⁴

The use of hydrogen fluoride.

Anhydrous hydrogen fluoride is an excellent solvent. Mixtures of alkali-metal, silver, thallous, magnesium, calcium or strontium fluorides with a Lewis acid such as boron trifluoride in HF result in the formation of the appropriate complex fluoride.⁴⁵ Presumably ammonium fluoride is soluble in hydrogen fluoride and a whole range of unknown ammonium salts could be prepared in this solvent. Many complex fluorides of divalent metal cations [e.g. Cu(II) , Mn(II)] can be prepared.⁴⁶

Hydrogen fluoride has the advantage that it is a non-oxidative solvent and complex fluorides of a lower oxidation state can be prepared. Reactions can be carried out in stainless steel bombs as there is no attack on the metal provided moisture is excluded.

Potassium bifluoride is a convenient source of hydrogen fluoride at high temperatures and one application of this reagent is the preparation of K_2ReF_6 by heating a

mixture of potassium bifluoride and ammonium iodorhenate.⁴⁹

The use of sulphur dioxide as a solvent.

The use of sulphur dioxide as a solvent for the preparation of complex fluorides has been studied briefly. Passage of boron trifluoride through a suspension of silver fluoride in liquid sulphur dioxide gives AgBF_4 .⁵⁰ Similarly AgPF_6 can be prepared.

The iodide ion in liquid sulphur dioxide reduces the hexafluorides of molybdenum, tungsten and rhenium and in the presence of alkali-metal iodides complexes of Mo(V), W(V) and Re(V) can be obtained.^{51,52} In the presence of excess sodium iodide the complex NaMoF_6 is further reduced to Na_2MoF_6 .⁵³

Electrolytic oxidation methods.

As water is electrolysed at high potentials the possibilities of electrolytic oxidation in aqueous solutions are limited; however, electrolysis of a suspension of manganous fluoride in 40% aqueous hydrofluoric acid and addition of potassium bifluoride gives K_2MnF_6 .⁵⁴ Although much work has appeared on the electrolysis of organic compounds in anhydrous hydrogen fluoride there seem to be no publications on the

application of this method for the preparation of complex fluorides.⁴³

Characterisation of complex fluorides.

Complex fluorides are generally insoluble, highly moisture sensitive compounds which do not sublime and which cannot be crystallised from any solvents. Their purification therefore presents a difficulty and the choice of starting materials for the preparation of a particular complex is very important.

X-ray powder photography is a very useful technique for the characterisation of complex fluorides. Most complex fluorides have simple powder patterns and the actual structure of a given complex appears to be determined mainly by geometrical considerations, ions of similar sizes crystallising in the same structural type. Thus the structure of a compound which has not been prepared previously can be predicted with a high degree of certainty. In the present work all the complex fluorides prepared have been characterised by their X-ray powder pattern.

Recently⁵³ infrared spectroscopy has been used as a method of characterising complex fluorides. Stretching

frequencies of a number of complex fluorides have been recorded so that information about structure and valency may be obtained. The spectra are easily recorded in nujol mulls which is satisfactory even for highly water sensitive compounds.

Magnetic measurements of complex fluorides are sometimes useful though this technique has not been used at all in this work. The use of quantitative measurements of paramagnetic susceptibility for the determination of oxidation states from the number of unpaired electrons is not always reliable and this is especially so for the heavier transition elements, among which many factors beside oxidation state are important in determining magnetic moments.

The use of sulphur tetrafluoride.

In the present work it has been found that by using sulphur tetrafluoride it is possible to prepare alkali-metal, ammonium, thallous and silver(I) fluoroborates, hexafluorosilicates, hexafluorogermanates, hexafluorostannates, hexafluoroplumbates, hexafluorophosphates, hexafluoroarsenates, hexafluoroantimonates, hexafluorotitanates, hexafluoronioates, hexafluoro-

tantalates, hexafluoromolybdates(V), hexafluorotungstates(V) and hexafluorouranates(IV). (See Table V).

Preparation of binary fluorides with sulphur tetrafluoride.

Sulphur tetrafluoride is a versatile fluorinating agent for the preparation of binary fluorides from inorganic oxides and sulphides (Table III).

Table III

Reaction of sulphur tetrafluoride with some inorganic oxides or sulphides.

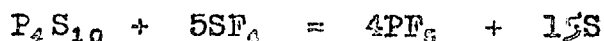
Reactant	Reaction Temperature	Products
$B_2O_3^a$	89-179°	BF_3SF_4
CO_2^b	500°	CF_4 , 80%; CoF_2 , 10%
CO^b	500°	CF_4 , 88%
GeO_2^a	100-300°	$GeF_4 \cdot 2SF_4$
SnS_2^a	300°	isolated as $SnF_4 \cdot 2HCONMe_2$
PbO_2^c	100°	PbF_2 (+ trace PbO_2)
NO_2^c	200-300°	$N_2O_2^+ SOF_3^-$
$P_4O_{10}^a$	100-250°	POF_3
$P_4S_{10}^a$	200-300°	$PF_5 + S$
$Bi_2O_3^a$	100-300°	BiF_3

Reactant	Reaction Temperature	Products
O_2^c	300°	no reaction
SO_2^a	50-150°	SOF_2
SO_3^a	50-150°	$S_2O_2F_2$, SO_2F_2 , SOF_2
SeO_2^a	100-240°	SeF_4
$I_2O_5^a$	60-150°	IF_5
CeO_2^c	100°	CeF_3
TiO_2^a	300°	isolated as $TiF_4 \cdot 2HCONMe_2$
$Nb_2O_5^d$	350	$NbF_5 \cdot 0.54SF_4$
$Ta_2O_5^d$	350°	$TaF_5 \cdot 0.39SF_4$
CrO_3^c	300°	contains 37.1% Cr, 60.5% F
$Mo(CO)_6^d$	165°	$MoF_5 \cdot 0.69SF_4$
MoO_3^a	70-350°	MoF_6
WO_3^a	350°	WF_6
MnO_2^c	300-350°	MnF_2 (+ trace MnO_2)
FeS_2^a	350°	FeF_3 + S
ZnS^a	60°	ZnF_2 + S (+ trace ZnS)
HgO^a	150°	HgF_2 + HgO
$UO_2^{d,e}$	350°	UF_4
$UO_3^{a,c}$	100-200°	UF_6

Reactant	Reaction Temperature	Products
$\text{UO}_2\text{F}_2^{\text{a}}$	400-425°	UF_6
$\text{U}_3\text{O}_8^{\text{a}}$	300-435	UF_4 , UF_6
UF_6^{c}	500°	UF_4
PuO_2^{c}	500°	PuF_4
PuF_6^{c}	500°	PuF_4

^a Oppegard, Smith, Muetterties and Englehardt,
 J. Amer. Chem. Soc., 1960, 82, 3835; ^b Hasek, Smith
 and Englehardt, *ibid*, 1960, 82, 543; ^c Smith and
 Engelhardt, *ibid*, 1960, 82, 3838; ^d Present work;
^e Johnson, Fischer and Steindler, J. Amer. Chem. Soc.,
 1961, 83, 1620.

This general reaction is characterised by replacement
 of the oxygen or sulphur to give the corresponding
 fluorides or in some cases, the corresponding oxyfluorides
 e.g.



An exception to this class of reactions is the oxidation of sulphur tetrafluoride to sulphur hexafluoride and sulphur oxytetrafluoride by strong oxidising agents such as nitrogen dioxide or chromium trioxide.⁵⁶

In contrast to the reactions of sulphur tetrafluoride with sulphides the reaction with oxides generally does not consume all of the fluorine bonded to the sulphur and therefore the sulphide fluorination would appear, at first glance, to be a superior reaction. However, because a number of elements do not form sulphides in the higher oxidation state such fluorides as iodine pentafluoride cannot be obtained by a sulphide fluorination. Also fluorination with sulphides result in the product being contaminated with a large amount of sulphur. This latter defect can be overcome by washing the sulphur out with carbon disulphide but this is not a good procedure when highly hygroscopic fluorides are being handled. The merits in the sulphide fluorination lie in the complete utilization of the fluoride and the observed fact that fluorination does not stop short of complete replacement as it does in the case of some oxides e.g. P_4O_{10} .

The main disadvantage with a number of preparations of binary fluorides with sulphur tetrafluoride is the formation of sulphur tetrafluoride complexes e.g.

$\text{BF}_3 \cdot \text{SF}_4$. However, a number of fluorides do not form sulphur tetrafluoride complexes¹⁰ e.g. SiF_4 , PF_5 , SeF_4 , IF_5 , MoF_6 , WF_6 , UF_4 and UF_6 and these compounds can be obtained pure.

Preparation of complex fluorides with sulphur tetrafluoride.

Sulphur tetrafluoride converts mixtures of alkali-metal fluorides and metal oxides, sulphides and carbonyls into complex fluorides (See Table V). Sulphur tetrafluoride is a particularly convenient reagent since the other product from the reaction with oxides is thionyl fluoride which is volatile and there is no solvolysis such as occurs when other non-aqueous fluorinating solvents (bromine trifluoride, iodine pentafluoride, selenium tetrafluoride etc.) are used. Sulphur tetrafluoride also has the advantages that it may be prepared without the use of elementary fluorine³⁶ and that the reactants are not necessarily oxidised to the maximum valency state.

All sulphur tetrafluoride adducts are unstable in the presence of basic fluorides: the fluoride ion is a better Lewis base than sulphur tetrafluoride. The decomposition of $\text{SF}_4 \cdot \text{BF}_3$ with potassium fluoride yields potassium fluoroborate and has been suggested as a method of preparing pure sulphur tetrafluoride.²⁵

Preparation of alkali-metal salts.

Lithium salts are easily prepared by use of sulphur tetrafluoride. LiNbF_6 and LiTaF_6 have been prepared previously in bromine trifluoride by Cox⁵⁷ but he was unable to index these isomorphous salts. These compounds have now been indexed and they are isomorphous with NaOsF_6 ⁶⁰ which has a rhombohedral lattice. LiMoF_6 has been prepared by fluorination of a 1:1 mixture of lithium fluoride and molybdenum carbonyl. This also has the NaOsF_6 structure. Attempts to prepare LiWF_6 by fluorination of various mixtures of lithium fluoride and tungsten carbonyl were unsuccessful.

Sodium, potassium and caesium salts of complex fluorides have been prepared with sulphur tetrafluoride. No rubidium salt has been isolated but there is no reason why salts of this metal could not be prepared.

Preparation of ammonium salts.

Fluorination of a 2:1 mixture of ammonium fluoride and boric oxide with sulphur tetrafluoride at 180° gave ammonium fluoroborate. This is the first reported method for the preparation of an ammonium salt in which a reasonably high temperature fluorinating method has been used. Previously ammonium salts have been prepared in aqueous hydrofluoric acid or by the reaction of ammonium fluoride with a metal bromide in anhydrous methanol.⁵⁹ Sulphur tetrafluoride reacts with ammonium fluoride at 200° to give a mixture of volatile and involatile products which have not been identified, however, in the preparation of ammonium fluoroborate it appeared that there was no attack on the ammonium ion. Few ammonium salts of pentavalent metal fluorides are known and the preparation of these salts has been left for a future study. The best method for preparing ammonium salts will probably be to dissolve a mixture of ammonium fluoride and a metal fluoride in anhydrous hydrogen fluoride and then remove the excess solvent under vacuum.

Preparation of thallous salts.

Both fluorine and bromine trifluoride oxidise thallium(I) to thallium(III) so that thallous salts cannot be prepared with these reagents. Thallous fluoride is soluble in selenium tetrafluoride and the compounds TlRuF_6^{24} and TlAsF_6^{44} have been prepared in this solvent. The products from the preparations involving selenium tetrafluoride contain selenium tetrafluoride and the use of sulphur tetrafluoride is easily the best method for preparing thallous salts. In the present work the new compounds TlNbF_6 , TlTaF_6 and TlMoF_6 have been prepared. The ionic radii of the thallous ion is similar to that of the rubidium ion and the above salts are all isomorphous with the corresponding rubidium salts.

Preparation of silver salts.

Attempts to prepare silver fluoride by fluorination of silver oxide or sulphide with sulphur tetrafluoride at various temperatures were only partly successful. The reactions never went to completion and the products were always a mixture of the starting material plus some silver fluoride.

Similarly attempts to prepare silver fluoroborate by fluorinating silver borate with sulphur tetrafluoride led

to products which were mixtures of silver borate and silver fluoroborate. However, silver fluoroborate was readily prepared by fluorination of a 2:1 mixture of silver fluoride and boric oxide at 175°. Other salts prepared were the previously unknown Ag_2GeF_6 and AgMoF_6 . Both these compounds were soluble in ether, benzene and toluene.

Preparation of calcium salts.

Calcium salts could not be prepared with sulphur tetrafluoride. Fluorination of a 1:1 mixture of calcium fluoride and germanium dioxide gave CaF_2 plus $\text{GeF}_4 \cdot 2\text{SF}_4$. Presumably sulphur tetrafluoride is a stronger Lewis base than calcium fluoride.

Preparation of hexafluorostannates and hexafluoroplumbates.

Fluorination of a 2:1 mixture of either sodium fluoride and stannic oxide or sodium fluoride and stannic sulphide with sulphur tetrafluoride gave products which had identical X-Ray powder patterns. The photographs can be indexed on an orthorhombic unit cell ($a = 4.50$, $b = 5.80$, $c = 10.1$). The compound from the oxide fluorination analyses as Na_2SnF_6 and an infrared spectrum of the solid in nujol gives a band at 552 cm^{-1} which

is characteristic of the SnF_6^{2-} anion.⁶⁵

Similarly fluorination of a 2:1 mixture of sodium fluoride and lead dioxide gives a white solid which rapidly becomes brown in moist air and gives a compound which is isomorphous with Na_2SnF_6 ($a = 4.55$, $b = 5.83$, $c = 10.1$) and analyses as Na_2PbF_6 . Both these compounds of previously unknown structure are isomorphous with Na_2PrF_6 ⁶⁰ ($a = 5.54$, $b = 3.97$, $c = 11.57$). Na_2ReF_6 can be indexed very satisfactorily on this orthorhombic cell although it has previously been regarded as tetragonal.⁴⁹

Preparation of fluoromolybdates(V) and fluorotungstates(V).

Most of the complexes resulting from the fluorinations of mixtures of alkali-metal fluorides and metal oxides and sulphides with sulphur tetrafluoride contain elements in the same valency state as the starting materials. However, fluorination of a 2:1 mixture of alkali metal fluorides and molybdenum carbonyl, dioxide or disulphide gave molybdenum(V) complexes and no tetravalent salts were obtained. It has previously been reported¹⁰ that fluorination of molybdenum disulphide gives molybdenum tetrafluoride which was characterised as its dimethyl sulphoxide adduct. It is likely that the actual product

from the fluorination of molybdenum disulphide is $\text{MoF}_5 \cdot \text{SF}_4$ (molybdenum tetrafluoride would most probably form a 1:2 adduct with sulphur tetrafluoride) and that this dissociates and disproportionates to MoF_4 and MoF_6 in solution with dimethyl sulphoxide. Similar disproportionation occurs when molybdenum pentachloride forms complexes with oxygen containing ligands.⁶¹ The action of sulphur tetrafluoride on a mixture of alkali-metal fluoride and tungsten carbonyl also gives pentavalent complexes. The infrared spectrum confirmed that the molybdenum and tungsten compounds were pentapositive.

Discussion of some of the X-ray results.

A discussion⁶² of the occurrence of the structures of potassium hexafluorosilicate (cubic), potassium hexafluorogermanate (trigonal) and potassium hexafluoromanganate (hexagonal) among complex fluorides of the formula A_2BF_6 (where A is a large cation) has led to the conclusion that the distribution is to a first approximation random, and that the distribution of structures cannot be satisfactorily interpreted solely on radius ratio effects. However, when A is a small cation such as sodium, radius ratio effects do seem important (see Table IV).

Table IV.

Structures and ionic radii of $\text{Na}_2\text{M}^{\text{IV}}\text{F}_6$ compounds.

Compound	Ionic crystal radii ($\text{\AA}$) ^g	Structure
Na_2SiF_6 ^a	0.41	H; $a = 8.86$, $c = 5.02$
Na_2GeF_6 ^a	0.53	H; $A = 9.10$, $c = 5.13$
Na_2TiF_6 ^a	0.64	H; $a = 9.21$, $c = 5.15$
Na_2MnF_6 ^a	0.66 (Mn^{3+})	H; $a = 9.03$, $c = 5.15$
Na_2IrF_6 ^b	0.66	H; $a = 9.34$, $c = 5.14$
Na_2PtF_6 ^a	0.83 (Pt^{5+})	H; $a = 9.41$, $c = 5.16$
Na_2SnF_6 ^c	0.71	O; $a = 4.50$, $b = 5.80$, $c = 10.1$
Na_2PbF_6 ^c	0.84	O; $a = 4.55$, $b = 5.83$, $c = 10.1$
Na_2ReF_6 ^c	0.78 (Re^{5+})	O; $a = 5.03$, $b = 5.81$, $c = 10.1$
Na_2PrF_6 ^e	0.99	O; $a = 5.54$, $b = 3.97$, $c = 11.57$
$\gamma\text{-Na}_2\text{UF}_6$ ^f	0.93	O; $a = 5.56$, $b = 4.01$, $c = 11.64$

^a Cox, J., 1954, 3251; ^b Hepworth, Robinson and Westland, J., 1958, 611; ^c Present work; ^e Asprey and Keenan, J. Inorg. Nucl. Chem., 1961, 16, 260; ^f Zachariasen, J. Amer. Chem. Soc., 1948, 70, 2147;
H; hexagonal; O, orthorhombic; ^g ionic radii from Kleinberg, Argersinger and Griswold, "Inorganic Chemistry", Heath and Co., Boston, 1960, p.75.

Thus compounds which have a tetravalent metal ion whose ionic radius is less than about 0.70Å crystallise with a hexagonal structure. Na_2ReF_6 has previously been indexed on a tetragonal unit cell⁴⁹ ($a = 10.02$, $c = 10.14$). However, in the present work this compound has been found to be isostructural with Na_2SnF_6 and Na_2PbF_6 and has been indexed on an orthorhombic unit cell. This latter structure is to be preferred since it gives a much smaller cell size for the compound.

Radius ratio effects also seem to be important in the structures of thallous salts. Thus the compounds prepared in the present work namely TlNbF_6 , TlTaF_6 and TlMoF_6 are all isomorphous with TlSbF_6 and TlAsF_6 .⁵⁴ These compounds all have rhombohedral deformed caesium chloride structures and are isomorphous with barium fluorosilicate. The only other known thallous salt of the general formula ABF_6 , i.e. TlPF_6 ⁵⁴, is cubic.

EXPERIMENTAL

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Preparation of alkali-metal fluorides.

Lithium fluoride. Lithium fluoride was prepared from "AnalaR" 40% hydrofluoric acid and "AnalaR" lithium carbonate and was dried at 300° before use.

Sodium fluoride. "AnalaR" sodium fluoride was used as supplied and was dried at 300° before use.

Potassium fluoride. Potassium fluoride was prepared from "AnalaR" 40% hydrofluoric acid and "AnalaR" potassium carbonate and was dried at 300° before use.

Caesium fluoride. Caesium fluoride was prepared from "AnalaR" 40% hydrofluoric acid and caesium carbonate and was dried at 300° before use.

Thallous fluoride. Thallous fluoride was prepared from "AnalaR" 40% hydrofluoric acid and thallous carbonate and was dried at 200° before use.

Ammonium fluoride. "AnalaR" ammonium fluoride was used from a new bottle.

Silver fluoride. Silver fluoride was prepared by the method of Anderson, Bak and Hillebert.⁶⁵ "AnalaR" 40% hydrofluoric acid was added dropwise to 5 g. of silver carbonate in a platinum dish until the carbonate was

neutralised. Any excess acid was removed by addition of a slight excess of silver carbonate and the reaction was completed by heating on a steam bath for half an hour. The solution was evaporated to small bulk and was filtered into 10 ml. of anhydrous methanol which was rapidly poured into 300 mls. of sodium dried ether. When the silver fluoride had settled the supernatant liquid was decanted into another 300 mls. of dry ether and this procedure of decantation and precipitation was repeated until no more silver fluoride was precipitated. The beakers containing the silver fluoride were placed in the dry box as soon as was possible and the silver fluoride was transferred to a flask. The last traces of ether were removed under vacuum at 60°. A golden yellow product was obtained which was stored in the dry box and was protected from light.

Preparation of metal oxides and sulphides.

Stannic sulphide. Stannic sulphide was prepared from tin, sulphur and ammonium chloride.⁶⁶

Molybdenum dioxide. The molybdenum dioxide used was a sample kindly supplied by Mr. K. C. Moss. It was prepared by reduction of molybdenum trioxide with hydrogen

at 470° for 36 hours. The product was washed with 6NHCl, water, 6NNH₄OH, water, acetone and dried at 130°.

Other metal oxides and sulphides. Niobium pentoxide, tantalum pentoxide and molybdenum disulphide were kindly supplied by Murex and Co. Ltd. The other metal oxides and sulphides were of ordinary reagent grade and were dried for 3 hours at 130°.

Metal carbonyls. Chromium, molybdenum and tungsten carbonyls were kindly supplied by Professor G. Wilkinson and were resublimed before use.

Use of sulphur tetrafluoride.

Sulphur tetrafluoride was used directly from cylinders of the gas which were kindly supplied by E. I. du Pont de Nemours and Co. Inc. and Imperial Chemical Industries Ltd.

All reactions in this work were carried out in a stainless steel bomb which was not attacked by sulphur tetrafluoride even at temperatures as high as 450°. A few reactions were attempted in Carius tubes before a bomb was available but these were unsatisfactory as the pyrex glass was attacked. Fluorinations with sulphur tetrafluoride can be carried out in a flow system at atmospheric pressure.¹⁰ The apparatus can be constructed

of pyrex glass since only minor etching is said to occur below 300° if the system is carefully dried and protected from moisture. However, at about 350°, sulphur tetrafluoride attacks glass with the formation of $\text{SF}_4 \cdot \text{BF}_3$, S and SF_6 .²¹

Preparation of complex fluorides.

Alkali fluoride-metal oxide, sulphide or carbonyl mixtures in various ratios (see Table V) were intimately mixed in an agate mortar and were placed in a dry 15 ml. stainless steel bomb fitted with a valve which could withstand high pressures. Mixtures which contained hygroscopic materials such as potassium fluoride or silver fluoride were handled in a dry-box. The bomb was evacuated, cooled in liquid nitrogen and an excess of sulphur tetrafluoride was condensed into the bomb which was subsequently rocked and heated overnight. The gaseous products were pumped off and the solid complexes were subsequently handled in the dry box. All the solid products were analysed and results are given in Table (V).

Table V.

Preparation of complex fluorides with sulphur tetrafluoride.

Reactants	Reaction Temp.	Solid Products	Analysis (%)	
			Found	Calc.
2KF:1B ₂ O ₃	200°	KBF ₄	BF ₄ , 68.1	BF ₄ , 69.0
2AgF:1B ₂ O ₃	175°	AgBF ₄	Ag, 54.5	Ag, 55.4
2NH ₄ F:1B ₂ O ₃	180°	NH ₄ BF ₄	BF ₄ , 83.6	BF ₄ , 82.8
2NaF:1SiO ₂	350°	Na ₂ SiF ₆	Si, 14.0	Si, 14.8
2NaF:1GeO ₂	350°	Na ₂ GeF ₆	Ge, 30.1	Ge, 31.2
2AgF:1GeO ₂	155°	Ag ₂ GeF ₆	Ag, 52.9	Ag, 53.6
2NaF:1SnS ₂	350°	Na ₂ SnF ₆ , S		
2NaF:1SnO ₂	350°	Na ₂ SnF ₆	Sn, 42.9	Sn, 42.6
2NaF:1PbO ₂	350°	Na ₂ PbF ₆	Pb, 56.0	Pb, 56.4
2NaF:1P ₂ S ₅	350°	NaPF ₆ , S		
2KF:1As ₂ O ₃	350°	KAsF ₆	As, 33.8	As, 32.9
2NaF:1Sb ₂ O ₃	350°	NaSbF ₆	Sb, 46.3	Sb, 47.1
2NaF:TiO ₂	350°	Na ₂ TiF ₆	Ti, 22.9	Ti, 23.1
2LiF:1Nb ₂ O ₅	350°	LiNbF ₆	Nb, 43.6	Nb, 43.4
2NaF:1Nb ₂ O ₅	350°	NaNbF ₆	Nb, 39.8	Nb, 40.4
2TlF:1Nb ₂ O ₅	350°	TlNbF ₆	Nb, 23.1	Nb, 22.6
2LiF:1Ta ₂ O ₅	350°	LiTaF ₆	Ta, 59.3	Ta, 59.9
2NaF:1Ta ₂ O ₅	350°	NaTaF ₆	Ta, 56.1	Ta, 56.9
2TlF:1Ta ₂ O ₅	350°	TlTaF ₆	Ta, 36.6	Ta, 36.2
1LiF:1Mo(CO) ₃	165°	LiMoF ₆	Mo, 44.5	Mo, 44.2

Reactants	Reaction Temp.	Solid Products	Analysis (%) Found	Calc.
2NaF:1Mo(CO) ₆	200°	NaMoF ₆ , NaF	Mo, 34.1	Mo, 34.9
2NaF:1MoO ₂	250°	NaMoF ₆ , NaF		
2NaF:1MoS ₂	400°	NaMoF ₆ , NaF MoS ₂ , S		
1CsF:1Mo(CO) ₆	200°	CsMoF ₆	Mo, 29.5	Mo, 28.0
1TlF:1Mo(CO) ₆	165°	TlMoF ₆	Mo, 24.0	Mo, 23.2
1AgF:1Mo(CO) ₆	155°	AgMoF ₆	Ag, 33.8	Ag, 33.9
2NaF:1W(CO) ₆	200°	NaWF ₆ , NaF	W, 50.1	W, 50.7
1CsF:1W(CO) ₆	200°	CsWF ₆	W, 41.9	W, 42.7
2NaF:1UO ₂	350°	Na ₂ UF ₆	U, 60.1	U, 59.8

Reaction of sulphur tetrafluoride with a 1:1 mixture of CaF₂ and GeO₂ at 250° gave a product which fumed in the dry box. This was clearly a mixture of CaF₂ and GeF₄·2SF₆.

X-Ray powder photographs of all the complexes prepared sealed in Lindemann glass capillaries were taken with Cu-Kα or Co-Kα radiation. The Lindemann glass capillaries were filled in a dry box and were sealed with warm picein wax. Measured values of sin² θ were compared with values obtained from lattice constants recorded in the literature for known compounds.

The X-ray data is recorded at the end of this chapter. No data is recorded for Ag_2GeF_6 or AgMoF_6 as the products were not crystalline and gave blank photos. The photo of Na_2UF_6 was very complicated and indicated that a number of phases were present. Na_2ReF_6 was re-indexed from $\sin^2 \theta$ values kindly supplied by Dr. R. D. Peacock.

Reaction of sulphur tetrafluoride with silver oxide and sulphide.

Reaction of sulphur tetrafluoride with either silver oxide or sulphide at temperatures of 200 and 350°, in each case yielded a product part of which was soluble in water. Evidence for solubility was obtained by precipitation of AgCl by addition of 2NHCl to the solution.

Reaction of sulphur tetrafluoride with silver borate.

Sulphur tetrafluoride and silver borate were heated in a Carius tube overnight at 140°. The product was partly soluble in water and an X-ray photo indicated that some silver fluoroborate was present.

Reaction of sulphur tetrafluoride with uranium dioxide.

Sulphur tetrafluoride fluorinated uranium dioxide at 350° to give UF_4 . Found: U, 75.1, UF_4 requires U, 75.8%.

Solubility of silver salts.

The compounds Ag_2GeF_6 and AgMoF_6 were soluble in ether, benzene and toluene. Evidence for solubility was obtained by the addition of 2NHCl to a clear solution of the compound. A white precipitate of silver chloride indicated that silver ions were in solution. Further evidence for the solubility of Ag_2GeF_6 in ether was obtained by the formation of a yellow precipitate when trityl chloride in ether was added to an ether solution of Ag_2GeF_6 . This yellow precipitate is characteristic of the formation of a triphenylmethyl carbonium salt.⁶⁷ The yellow compound was not isolated and analysed. It may have been either $(\text{Ph}_3\text{C})_2\text{GeF}_6$ or $\text{Ph}_3\text{C}.\text{GeF}_6$.

Table VI.

The infrared spectra data of some complex fluorides.

<u>Compound</u>	<u>Absorption</u>	<u>Lit. value.</u> ⁵⁸
Na_2SnF_6	552 cm^{-1}	552 cm^{-1}
LiNbF_6	578	580
LiTaF_6	577	580
LiMoF_6	625	623
NaMoF_6	626	623
NaWF_6	597	594

X-ray data for KBF_4 .Cu-K α radiation.

<u>Intensity</u>	<u>d($\text{\AA}$)</u>	<u>$\sin^2\theta(\text{obs.})$</u>	<u>(h,k,l)</u>	<u>$\sin^2\theta(\text{calc.})$</u>
w	3.824	0.0405	200	0.0387
s	3.385	0.0518	201	0.0496
			102	0.0534
m	3.234	0.0567	210	0.0571
s	3.039	0.0641	012	0.0622
s	2.785	0.0759	020	0.0737
m	2.456	0.0999	301	0.0980
			003	0.0985
			212	0.0999
m	2.305	0.1116	220	0.1124
s	2.190	0.1237	221	0.1233
s	2.070	0.1384	203	0.1371
m	1.998	0.1485	312	0.1492
vw	1.922	0.1604	320	0.1607
w	1.807	0.1814	123	0.1818
w	1.756	0.1923	014	0.1935
m	1.583	0.2367	421	0.2394
w	1.543	0.2490	232	0.2482
			024	0.2487

<u>Intensity</u>	<u>$d(\text{\AA})$</u>	<u>$\sin^2\theta(\text{obs.})$</u>	<u>(h,k,l)</u>	<u>$\sin^2\theta(\text{calc.})$</u>
m	1.509	0.2602	323	0.2592
			510	0.2602
			304	0.2621
m	1.388	0.3081	041	0.3057
m	1.360	0.3206	430	0.3205
vw	1.314	0.3434	241	0.3443
vw	1.291	0.3553	125	0.3569
mw	1.234	0.3894	602	0.3919
mw	1.196	0.4148	523	0.4139
			504	0.4168
vw	1.174	0.4307	405	0.4282
			243	0.4319
vw	1.162	0.4394	035	0.4393
w	1.138	0.4580	441	0.4604

Crystal Symmetry: Orthorhombic¹⁴⁸

Lattice constants: $a = 7.84\text{\AA}$; $b = 5.68\text{\AA}$; $c = 7.37\text{\AA}$.

X-ray data for AgBF₄.Co K α radiation.

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
m	4.136	0.0468	-	-
w	4.024	0.0495	200	0.0519
m	3.675	0.0591	002	0.0616
w	3.451	0.0671	201	0.0689
w	3.349	0.0713	201	0.0689
s	3.205	0.0779	102	0.0758
m	3.093	0.0836	-	-
s	2.894	0.0956	211	0.0950
m	2.688	0.1120	-	-
m	2.644	0.1143	202	0.1157
vw	2.502	0.1276	-	-
mw	2.324	0.1479	310	0.1460
m	2.216	0.1627	311	0.1616
w	2.158	0.1716	221	0.1732
s	2.104	0.1806	122	0.1800
m	2.018	0.1964	-	-
m	2.001	0.1995	-	-
s	1.955	0.2090	312	0.2084

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
m	1.939	0.2125	400	0.2131
m	1.889	0.2236	320	0.2242
vw	1.856	0.2324	030	0.2346
vw	1.812	0.2436	023	0.2448

Crystal Symmetry: Orthorhombic¹⁴³

Lattice constants: $a = 7.75\text{\AA}$; $b = 5.54\text{\AA}$; $c = 7.16\text{\AA}$.

X-ray data for NH_4BF_4 .Cu-K α radiation.

<u>Intensity</u>	<u>d($\text{\AA}$)</u>	<u>$\sin^2\theta$(obs.)</u>	<u>(h,k,l)</u>	<u>$\sin^2\theta$(calc.)</u>
m	5.68	0.0183	010	0.0184
			101	0.0189
s	5.489	0.0295	011	0.0298
			200	0.0301
ms	3.860	0.0392	111	0.0373
			201	0.0415
m	3.661	0.0443	002	0.0457
s	3.551	0.0470	210	0.0485
vw	3.392	0.0516	102	0.0532
s	3.185	0.0584	211	0.0599
s	2.910	0.0700	300	0.0676
			112	0.0716
m	2.833	0.0740	112	0.0716
		0.0740	020	0.0736
			202	0.0757
s	2.539	0.0920	121	0.0926
			212	0.0941
w	2.407	0.1023	003	0.1028
			220	0.1037

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
s	2.332	0.1090	103	0.1103
m	2.289	0.1131	302	0.1133
m	2.233	0.1189	022	0.1193
s	2.169	0.1261	122	0.1268
w	2.107	0.1336	203	0.1328
vw	2.007	0.1472	222	0.1494
vw	1.888	0.1663	030	0.1657
			402	0.1659
m	1.813	0.1803	004	0.1827
m	1.719	0.2008	501	0.1993
			014	0.2011
w	1.678	0.2107	204	0.2128
s	1.651	0.2174	511	0.2177

Crystal Symmetry: Orthorhombic^{144, 145}

Lattice constants: $a = 8.89\text{\AA}$; $b = 5.68\text{\AA}$; $c = 7.21\text{\AA}$.

X-ray data for Na₂SiF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
m	4.480	0.0296	110	0.0303
s	4.251	0.0328	101	0.0337
s	3.351	0.0528	111	0.0539
s	3.072	0.0629	201	0.0640
s	2.919	0.0696	210	0.0707
w	2.522	0.0932	211	0.0943
			002	0.0944
m	2.284	0.1132	301	0.1145
s	2.214	0.1210	220	0.1212
w	2.119	0.1321	310	0.1313
w	2.034	0.1433	221	0.1448
w	1.963	0.1536	311	0.1549
m	1.906	0.1632	400	0.1616
			212	0.1651
m	1.777	0.1876	401	0.1852
			302	0.1853
s	1.665	0.2138	003	0.2124
			321	0.2155
			220	0.2156

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
w	1.626	0.2240	103	0.2225
			312	0.2257
s	1.595	0.2344	411	0.2357
m	1.527	0.2541	203	0.2528
			402	0.2560
s	1.476	0.2720	330	0.2727
w	1.453	0.2810	420	0.2828
m	1.396	0.3049	303	0.3033
			421	0.3064

Crystal Symmetry: Hexagonal¹³¹

Lattice constants: $a = 8.86\text{\AA}$; $c = 5.02\text{\AA}$.

X-ray data for Na₂GeF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
s	4.541	0.0288	110	0.0287
s	4.280	0.0324	101	0.322
s	3.392	0.0516	111	0.0513
s	3.108	0.0614	201	0.0608
m	2.619	0.0866	300	0.0860
s	2.560	0.0905	002	0.0904
s	2.327	0.1095	301	0.1086
w	2.268	0.1151	220	0.1147
w	2.144	0.1290	202	0.1286
w	2.067	0.1389	221	0.1373
w	1.999	0.1483	311	0.1469
w	1.929	0.1593	212	0.1573
s	1.825	0.1780	401	0.1756
			302	0.1764
s	1.693	0.2068	222	0.2051
w	1.654	0.2165	312	0.2147
m	1.628	0.2261	411	0.2234
w	1.558	0.2440	203	0.2416
			402	0.2434

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
m	1.506	0.2613	501	0.2616
m	1.472	0.2735	322	0.2720
m	1.419	0.2940	510	0.2964

Crystal Symmetry : Hexagonal¹⁵¹

Lattice constants : $a = 9.10\text{Å}$; $c = 5.13\text{Å}$.

X-ray data for Na_2SnF_6 ($2\text{NaF}:1\text{SnS}_2/\text{SF}_6$).

Cu-K α radiation.

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
10	5.079	0.0230	011	0.0236
			002	0.0236
9	4.489	0.0295	100	0.0293
9	3.561	0.0469	110	0.0470
4	2.899	0.0707	112	0.0706
			020	0.0707
			013	0.0707
4	2.782	0.0768	021	0.0766
2	2.513	0.0941	022	0.0942
			004	0.0942
3	2.438	0.1000	120	0.1000
			113	0.1000
3	2.249	0.1175	200	0.1174
3	2.191	0.1238	201	0.1233
			122	0.1236
			104	0.1236
			023	0.1237
2	2.052	0.1411	211	0.1409
			202	0.1409
			114	0.1413

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
9	1.869	0.1701	203	0.1704
7	1.780	0.1875	220	0.1880
			213	0.1880
			130	0.1884
7	1.679	0.2107	222	0.2116
			204	0.2116
5	1.590	0.2351	-	-
8	1.518	0.2580	116	0.2591
8	1.502	0.2633	300	0.2641
			205	0.2646
2	1.453	0.2813	310	0.2817
3	1.399	0.3037	312	0.3053
2	1.383	0.3106	140	0.3121
			126	0.3121
5	1.347	0.3276	233	0.3294
			206	0.3294
5	1.291	0.3568	322	0.3583
			304	0.3583
3	1.261	0.3738	314	0.3760
2	1.223	0.3972	-	-
3	1.214	0.4032	-	-
2	1.189	0.4204	-	-

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
2	1.158	0.4428	050	0.4418
2	1.150	0.4492	051	0.4476
			037	0.4476
			028	0.4476
2	1.128	0.4674	052	0.4653
			400	0.4694
1	1.098	0.4928	411	0.4930
			402	0.4930
1	1.047	0.5420	420	0.5401
			413	0.5401
1	1.031	0.5588	250	0.5591
7	1.005	0.5880	00,10	0.5890
			055	0.5890
1	0.989	0.6076	01,10	0.6067
4	0.971	0.6299	430	0.6285

Crystal Symmetry : Orthorhombic

Lattice constants : $a = 4.50\text{Å}$; $b = 5.80\text{Å}$; $c = 10.1\text{Å}$.

X-ray data for Na₂PbF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
8	5.036	0.0234	011	0.0234
			002	0.0235
7	4.478	0.0296	100	0.0287
7	3.537	0.0475	110	0.0462
8	3.355	0.0528	111	0.0521
			102	0.0522
8	2.916	0.0699	112	0.0697
			020	0.0699
			013	0.0704
6	2.820	0.0748	021	0.0758
2	2.533	0.0926	022	0.0934
2	2.463	0.0986	120	0.0986
			113	0.0991
7	2.270	0.1154	200	0.1149
8	2.210	0.1216	201	0.1208
10	2.078	0.1371	211	0.1382
			202	0.1384
9	1.890	0.1663	015	0.1645
			203	0.1678

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
5	1.796	0.1842	220	0.1848
8	1.770	0.1898	221	0.1906
6	1.695	0.2070	222	0.2083
2	1.671	0.2128	006	0.2117
4	1.606	0.2305	016	0.2292
5	1.545	0.2489	034	0.2513
7	1.519	0.2576	116	0.2579
5	1.472	0.2742	230	0.2721
3	1.422	0.2941	232	0.2956
3	1.409	0.2991	312	0.2995
4	1.396	0.3050	035	0.3042
			017	0.3056
6	1.364	0.3193	107	0.3168
6	1.348	0.3268	206	0.3266
6	1.317	0.3425	216	0.3440
5	1.306	0.3485	-	-
1	1.287	0.3585	027	0.3580
2	1.270	0.3684	036	0.3689
3	1.239	0.3874	127	0.3867
2	1.225	0.3958	226	0.3964
2	1.212	0.4044	108	0.4050
			305	0.4055

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
5	1.201	0.4120	-	-
4	1.174	0.4314	-	-
5	1.163	0.4396	332	0.4392

Crystal Symmetry : Orthorhombic

Lattice constants : $a = 4.55\text{Å}$; $b = 5.83\text{Å}$; $c = 10.1\text{Å}$.

X-ray data for NaPF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h.k.l)</u>	<u>sin²θ(calc.)</u>
s	4.424	0.0304	111	0.0308
s	3.831	0.0404	200	0.0410
w	2.694	0.0817	220	0.0821
vw	2.626	0.0861	=	=
w	2.290	0.1131	311	0.1129
vw	2.113	0.1330	=	=
m	1.904	0.1634	400	0.1642
w	1.722	0.2001	331	0.1949
m	1.700	0.2051	420	0.2052
w	1.554	0.2455	422	0.2462
w	1.465	0.2763	333	0.2770
			511	0.2770
w	1.344	0.3286	440	0.3283
w	1.268	0.3691	600	0.3694
			442	0.3694
w	1.202	0.4106	620	0.4104

Crystal Symmetry : Cubic (face centred)^{87,148}Lattice constant : $a = 7.60\text{\AA}$.

X-ray data for KAsF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
m	4.808	0.0257	101	0.0260
m	3.691	0.0436	110	0.0440
w	3.182	0.0586	—	—
w	3.076	0.0627	102	0.0600
w	2.874	0.0718	201	0.0699
vw	2.638	0.0852	—	—
w	2.341	0.1082	202	0.1039
w	2.015	0.1404	—	—
vw	1.836	0.1756	220	0.1758
vw	1.812	0.1806	—	—
vvw	1.660	0.2147	—	—
vvw	1.597	0.2324	303	0.2339
vvw	1.551	0.2466	401	0.2457
w	1.456	0.2797	402	0.2798
vw	1.430	0.2898	321	0.2897
vw	1.355	0.3231	322	0.3237

Crystal Symmetry : Rhombohedral^{57, 147}Lattice constants : $a = 4.92\text{\AA}$; $\alpha = 97.2^\circ$.

X-ray data of NaSbF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d(Å²)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
s	4.706	0.0268	111	0.0266
s	4.086	0.0355	200	0.0355
m	2.897	0.0707	220	0.0709
m	2.470	0.0972	311	0.0976
m	2.044	0.1419	400	0.1419
w	1.872	0.1692	331	0.1685
m	1.826	0.1778	420	0.1774
m	1.677	0.2110	422	0.2128
m	1.574	0.2392	333	0.2394
			511	0.2394
m	1.442	0.2850	440	0.2838
m	1.385	0.3093	531	0.3104
m	1.364	0.3186	600	0.3193
			442	0.3193
w	1.292	0.3550	620	0.3547

Crystal Symmetry : Cubic (face centred)¹⁴⁸Lattice constant: $a = 8.18\text{Å}$.

X-ray data for Na₂TiF₆Cu-K α radiation.

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
w	4.951	0.0242	001	0.0224
m	4.604	0.0280	110	0.0280
m	4.296	0.0322	101	0.0317
m	3.431	0.0503	111	0.0504
m	3.145	0.0599	201	0.0597
w	2.597	0.0880	211	0.0877
			002	0.0896
m	2.356	0.1068	301	0.1064
m	1.839	0.1751	302	0.1773
m	1.717	0.2012	321	0.2016
			003	0.2016
w	1.644	0.2193	411	0.2183
w	1.529	0.2535	330	0.2519
			501	0.2557
w	1.480	0.2705	332	0.2744
w	1.437	0.2867	412	0.2855
			303	0.2856

Crystal Symmetry : Hexagonal¹⁸¹

Lattice constants : a = 9.21Å ; c = 5.15Å .

X-ray data for LiNbF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d($\text{\AA}$)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
m	4.564	0.0286	003	0.0290
vs	4.346	0.0315	101	0.0312
vs	3.818	0.0406	102	0.0409
m	3.443	0.0793	104	0.0796
ms	2.657	0.0840	110	0.0840
vw	2.430	0.1004	-	-
m	2.338	0.1085	105	0.1086
vs	2.290	0.1131	113	0.1130
w	2.182	0.1246	202	0.1249
w	1.987	0.1502	-	-
s	1.903	0.1637	204	0.1636
vw	1.844	0.1743	-	-
w	1.784	0.1862	107	0.1860
w	1.755	0.1928	205	0.1926
vs	1.722	0.1999	211	0.1992
			116	0.2001
ms	1.685	0.2089	212	0.2089
w	1.590	0.2340	108	0.2343
m	1.545	0.2482	214	0.2476

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
m	1.532	0.2526	300	0.2520
vw	1.509	0.2602	009	0.2611
w	1.481	0.2702	207	0.2700
m	1.463	0.2769	215	0.2766
w	1.452	0.2813	303	0.2810
m	1.364	0.3186	208	0.3183
w	1.327	0.3366	220	0.3360
m	1.309	0.3458	119	0.3451
m	1.296	0.3526	10,10	0.3504
			217	0.3540
m	1.275	0.3669	311	0.3672
m	1.253	0.3773	312	0.3769
mw	1.215	0.4021	218	0.4023
mw	1.192	0.4169	314	0.4156
			0.1,11	0.4181
mw	1.155	0.4446	315	0.4446
mw	1.145	0.4522	226	0.4521
mw	1.133	0.4626	20,10	0.4624
w	1.088	0.5010	20,11	0.5021

Crystal Symmetry : Rhombohedral

Lattice constants : $a = 5.47\text{Å}$; $\alpha = 58.2^\circ$.

X-ray data for NaNbF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
s	4.731	0.0265	111	0.0262
s	4.128	0.0348	200	0.0350
vw	3.072	0.0629	-	-
m	2.914	0.0699	220	0.0699
m	2.489	0.0958	311	0.0962
s	2.059	0.1399	400	0.1399
w	1.879	0.1661	331	0.1661
s	1.841	0.1749	420	0.1748
m	1.684	0.2092	422	0.2098
m	1.569	0.2407	333	0.2360
			511	0.2360
m	1.456	0.2797	440	0.2797
m	1.394	0.3051	531	0.3060
m	1.373	0.3143	600	0.3147
			442	0.3147
w	1.305	0.3482	620	0.3497
w	1.259	0.3742	533	0.3759
w	1.191	0.4171	444	0.4196
w	1.154	0.4453	711	0.4458
			551	0.4458

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
w	1.143	0.4538	640	0.4546
w	1.102	0.4883	642	0.4896
w	1.073	0.5149	553	0.5158
			731	0.5158

Crystal Symmetry : Cubic (face centred)⁵⁷

Lattice constant : a = 8.27Å .

X-ray data for TiNbF_6 .Cu-K α radiation.

<u>Intensity</u>	<u>d($\text{\AA}$)</u>	<u>$\sin^2\theta$(obs.)</u>	<u>(h,k,l)</u>	<u>$\sin^2\theta$(calc.)</u>
s	3.782	0.0414	110	0.0406
s	3.385	0.0518	102	0.0521
vw	2.644	0.0848	003	0.0867
m	2.537	0.0921	202	0.0927
m	2.378	0.1048	211	0.1044
m	2.202	0.1223	300	0.1218
s	2.112	0.1331	212	0.1333
ms	1.903	0.1636	220	0.1624
mw	1.706	0.2037	-	-
m	1.665	0.2136	312	0.2144
mw	1.558	0.2440	-	-
m	1.529	0.2533	105	0.2544
m	1.444	0.2842	410	0.2841
m	1.418	0.2946	205	0.2950
mw	1.349	0.3257	-	-
mw	1.274	0.3653	330	0.3653
mw	1.256	0.3759	502	0.3768
w	1.209	0.4055	-	-
w	1.194	0.4159	315	0.4168

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
m	1.139	0.4569	405	0.4574
w	1.105	0.4857	107	0.4857
w	1.091	0.4983	325	0.4980
w	1.062	0.5262	207	0.5263
w	1.052	0.5366	-	-
w	1.021	0.5686	217	0.5669
mw	0.9798	0.6179	425	0.6197
mw	0.9571	0.6477	317	0.6481

Crystal Symmetry : Rhombohedral

Lattice constants : $a = 5.13\text{\AA}$; $\alpha = 96.4^\circ$.

X-ray data for LiTaF_6 .Cu-K α radiation.

<u>Intensity</u>	<u>d($\text{\AA}$)</u>	<u>$\sin^2\theta(\text{obs.})$</u>	<u>(h,k,l)</u>	<u>$\sin^2\theta(\text{calc.})$</u>
m	4.515	0.0291	003	0.0290
vw	4.334	0.0316	101	0.0312
vs	3.811	0.0406	102	0.0409
m	2.731	0.0796	104	0.0796
m	2.652	0.0843	110	0.0840
m	2.333	0.1089	105	0.1086
s	2.290	0.1131	113	0.1130
w	2.262	0.1159	201	0.1152
			006	0.1161
w	2.181	0.1248	202	0.1249
s	1.903	0.1636	204	0.1636
w	1.787	0.1857	107	0.1860
w	1.756	0.1925	205	0.1926
s	1.724	0.1997	211	0.1992
			116	0.2001
m	1.684	0.2092	212	0.2089
w	1.591	0.2337	108	0.2343
mw	1.547	0.2478	214	0.2476
mw	1.531	0.2529	300	0.2520
vw	1.510	0.2599	-	-

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
w	1.483	0.2695	207	0.2700
w	1.464	0.2766	215	0.2766
w	1.454	0.2803	303	0.2810
w	1.366	0.3178	208	0.3183
w	1.327	0.3366	220	0.3360
w	1.312	0.3441	119	0.3451
w	1.293	0.3541	217	0.3540
m	1.270	0.3670	311	0.3672
mw	1.253	0.3773	312	0.3769
mw	1.215	0.4017	218	0.4023
mw	1.193	0.4165	314	0.4156
vw	1.170	0.4330	20,10	0.4344
w	1.154	0.4448	315	0.4446
w	1.145	0.4522	226	0.4521
w	1.134	0.4615	402	0.4609
w	1.089	0.5003	404	0.4996

Crystal Symmetry : Rhombohedral

Lattice constants : $a = 5.47\text{\AA}$; $\alpha = 58.2^\circ$.

X-ray data for NaTaF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
s	4.692	0.0269	111	0.0263
s	4.065	0.0358	200	0.0351
s	2.897	0.0707	220	0.0702
s	2.474	0.0969	311	0.0965
s	2.053	0.1407	400	0.1404
m	1.887	0.1666	331	0.1667
s	1.838	0.1754	420	0.1755
s	1.680	0.2101	422	0.2106
s	1.586	0.2358	333	0.2369
			511	0.2369
s	1.457	0.2794	440	0.2808
s	1.394	0.3052	531	0.3071
s	1.373	0.3143	600	0.3159
			442	0.3159
m	1.304	0.3490	620	0.3510
w	1.258	0.3747	533	0.3757
s	1.190	0.4180	444	0.4200

Crystal Symmetry : Cubic (face Centred)⁵⁷Lattice constant : $a = 8.26\text{\AA}$.

X-ray data for TlTaF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
s	3.804	0.0410	110	0.0404
s	3.410	0.0510	102	0.0518
ms	2.547	0.0914	202	0.0922
m	2.207	0.1217	300	0.1212
s	2.116	0.1325	122	0.1326
s	1.911	0.1624	220	0.1616
w	1.711	0.2026	-	-
m	1.667	0.2132	312	0.2134
mw	1.560	0.2436	-	-
mw	1.560	0.2532	105	0.2530
mw	1.446	0.2832	410	0.2829
mw	1.421	0.2933	205	0.2934
w	1.354	0.3232	-	-
vw	1.332	0.3339	215	0.3338
m	1.275	0.3642	330	0.3637
m	1.259	0.3742	502	0.3751
w	1.206	0.4075	324	0.4092
w	1.196	0.4144	315	0.4146
m	1.142	0.4549	405	0.4550

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
vw	1.105	0.4857	600	0.4849
vw	1.096	0.4940	325	0.4954
vw	1.064	0.5244	207	0.5233
vw	1.051	0.5380	432	0.5367
w	1.024	0.5651	217	0.5637
mw	0.9858	0.5936	-	-
mw	0.9588	0.6453	317	0.6445
			404	0.6466

Crystal Symmetry : Rhombohedral

Orthorhombic: $a = 5.14\text{\AA}$, $\alpha = 96.4^\circ$.

Cu-K α radiation.

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
s	4.561	0.0285	003	0.0288
s	3.680	0.0324	101	0.0325
s	3.750	0.0421	102	0.0421
vw	3.125	0.0608	-	-
vw	3.074	0.0628	-	-
ms	2.720	0.0802	104	0.0805
m	2.604	0.0875	110	0.0880
m	2.330	0.1092	105	0.1093
s	2.251	0.1167	113	0.1168
w	2.139	0.1296	202	0.1301
w	2.010	0.1466	-	-
s	1.868	0.1698	204	0.1685
mw	1.782	0.1867	107	0.1861
w	1.731	0.1980	205	0.1973
s	1.708	0.2033	116	0.2032
w	1.686	0.2087	211	0.2085
ms	1.650	0.2176	212	0.2181
w	1.588	0.2348	108	0.2341
m	1.522	0.2559	214	0.2565
m	1.500	0.2633	300	0.2640

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
m	1.469	0.2748	207	0.2741
m	1.441	0.2851	215	0.2853
m	1.421	0.2933	303	0.2928
m	1.354	0.3234	208	0.3221
ms	1.303	0.3495	119	0.3472
m	1.277	0.3632	217	0.3621
m	1.245	0.3826	223	0.3808
			311	0.3842
m	1.227	0.3941	312	0.3941
w	1.202	0.4104	218	0.4101

Crystal Symmetry : Rhombohedral

Lattice constants : $a = 5.44\text{Å}$, $\alpha = 57.0^\circ$.

X-ray data for $\text{NaMoF}_6(2\text{NaF}:1\text{Mo}(\text{CO})_6/\text{SF}_6)_x$.

Cu-K α radiation.

<u>Intensity</u>	<u>d($\text{\AA}$)</u>	<u>$\sin^2\theta(\text{obs.})$</u>	<u>(h,k,l)</u>	<u>$\sin^2\theta(\text{calc.})$</u>
s	4.792	0.0258	111	0.0266
s	4.128	0.0348	200	0.0355
s	2.914	0.0699	220	0.0710
w	2.767	0.0776	-	-
s	2.478	0.0966	311	0.0977
s	2.036	0.1430	400	0.1421
vw	1.996	0.1487	-	-
s	1.836	0.1756	420	0.1776
w	1.739	0.1962	-	-
s	1.680	0.2102	422	0.2131
vw	1.654	0.2165	-	-
s	1.581	0.2373	333	0.2397
			511	0.2397
s	1.447	0.2827	440	0.2841
s	1.383	0.3101	531	0.3108
s	1.365	0.3181	600	0.3196
			442	0.3196
w	1.292	0.3548	620	0.3552
w	1.247	0.3814	533	0.3818

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
w	1.233	0.3900	622	0.3907
w	1.185	0.4225	444	0.4262
w	1.086	0.4515	711	0.4528
			551	0.4528

Crystal Symmetry : Cubic (face centred)⁸²

Lattice constant : $a = 8.20\text{Å}$.

X-ray data for NaMoF₆(2NaF:1MoO₃/SF₆)₂Cu-K α radiation.

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc)</u>
s	4.471	0.0271	111	0.0266
s	4.073	0.0358	200	0.0355
vs	2.870	0.0721	220	0.0710
w	2.717	0.0804	-	-
m	2.453	0.0986	311	0.0977
vw	2.275	0.1144	-	-
s	2.035	0.1433	400	0.1421
s	1.819	0.1793	420	0.1776
m	1.663	0.2142	422	0.2131
m	1.568	0.2410	333	0.2397
			511	0.2397
m	1.4400	0.2854	440	0.2841
m	1.379	0.3114	531	0.3108
m	1.359	0.3208	600	0.3196
			442	0.3196
w	1.290	0.4621	640	0.4617
w	1.091	0.4986	642	0.4972

Crystal Symmetry : Cubic (face centred)⁵³Lattice constant : $a = 8.20\text{\AA}$.

X-ray data for NaMoF₆(2NaF:1MoS₂/SF₆)₂Cu-K α radiation.

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
s	4.711	0.0266	111	0.0266
s	4.086	0.0355	200	0.0355
s	2.887	0.0713	220	0.0710
m	2.487	0.0960	311	0.0977
m	2.042	0.1423	400	0.1421
s	1.825	0.1781	420	0.1776
vw	1.725	0.1992	-	-
w	1.665	0.2138	422	0.2131
s	1.575	0.2390	333	0.2397
			511	0.2397
w	1.444	0.2840	440	0.2841
w	1.379	0.3117	531	0.3108
m	1.361	0.3200	600	0.3196
			442	0.3196
s	1.294	0.3538	620	0.3552

Crystal Symmetry : Cubic (face centred)⁵²Lattice constant : $a = 8.20\text{\AA}$.

X-ray data for CsMoF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
m	3.887	0.0393	110	0.0384
m	3.571	0.0465	111	0.0474
m	3.469	0.0493	102	0.0486
w	2.598	0.0879	202	0.0820
w	2.247	0.1176	300	0.1153
m	2.159	0.1273	212	0.1254
w	2.040	0.1425	-	-
m	1.948	0.1562	220	0.1536
w	1.803	0.1822	-	-
w	1.736	0.1967	303	0.1957
w	1.698	0.2057	312	0.2023
w	1.587	0.2355	223	0.2340
w	1.558	0.2440	402	0.2403
vw	1.474	0.2726	-	-
w	1.446	0.2834	-	-
vw	1.398	0.3032	-	-
vw	1.376	0.3134	-	-
w	1.303	0.3491	413	0.3493
w	1.283	0.3600	420	0.3587

Crystal Symmetry : Rhombohedral^{6a}Lattice constants : $a = 5.29\text{\AA}$; $\alpha = 96.0^\circ$.

X-ray data for TlMoF_6 .Co-K α radiation.

<u>Intensity</u>	<u>d($\text{\AA}$)</u>	<u>$\sin^2\theta$(obs.)</u>	<u>(h,k,l)</u>	<u>$\sin^2\theta$(calc.)</u>
s	3.272	0.0555	110	0.0552
s	2.901	0.0705	102	0.0699
s	2.662	0.0837	201	0.0865
vw	2.248	0.1175	003	0.1158
m	2.175	0.1254	202	0.1251
m	2.043	0.1421	211	0.1416
m	1.903	0.1637	300	0.1655
w	1.859	0.1716	113	0.1710
s	1.810	0.1818	212	0.1802
w	1.639	0.2211	220	0.2207
w	1.471	0.2736	-	-
m	1.453	0.2808	303	0.2813
ms	1.429	0.2908	312	0.2906
s	1.329	0.3354	214	0.3346
			223	0.3365
m	1.240	0.3855	410	0.3862
s	1.216	0.4005	322	0.4009
m	1.154	0.4452	314	0.4550
w	1.131	0.4644	006	0.4633

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
w	1.095	0.4951	330	0.4965
w	1.089	0.5003	404	0.5001
w	1.078	0.5103	502	0.5113
w	1.069	0.5194	116	0.5185

Crystal Symmetry : Rhombohedral

Lattice constants : a = 5.12; α = 96.6°.

X-ray data for $\text{NaWF}_6 \cdot 12\text{NaF} \cdot 1\text{W}(\text{CO})_6$.Cu-K α radiation.

<u>Intensity</u>	<u>d($\text{\AA}$)</u>	<u>$\sin^2\theta(\text{obs.})$</u>	<u>(h,k,l)</u>	<u>$\sin^2\theta(\text{calc.})$</u>
s	3.579	0.0282	111	0.0266
s	3.991	0.0373	200	0.0355
s	2.840	0.0736	220	0.0710
s	2.453	0.0986	311	0.0976
m	2.259	0.1162	222	0.1165
m	2.035	0.1432	400	0.1420
vw	1.918	0.1612	-	-
m	1.832	0.1767	420	0.1774
s	1.664	0.2140	422	0.2129
vw	1.576	0.2387	511	0.2395
			333	0.2395
ms	1.444	0.2842	440	0.2839
m	1.383	0.3100	531	0.3105
m	1.363	0.3190	600	0.3194
w	1.292	0.3550	620	0.3549
w	1.145	0.4520	711	0.4525
			551	0.4525
w	1.136	0.4600	640	0.4613
vw	1.094	0.4960	642	0.4968
vw	1.065	0.5230	553	0.5236
			731	0.5236

Crystal Symmetry : Cubic (face centred)⁸²
 Lattice constant : $a = 8.18\text{\AA}$.

X-ray data for CsWF₆.Cu-K α radiation.

<u>Intensity</u>	<u>d($\text{\AA}$)</u>	<u>$\sin^2\theta$(obs.)</u>	<u>(h,k,l)</u>	<u>$\sin^2\theta$(calc.)</u>
w	5.193	0.0220	101	0.0215
m	3.911	0.0388	110	0.0384
m	3.525	0.0477	102	0.0476
s	3.136	0.0604	201	0.0599
mw	2.547	0.0194	-	-
w	2.254	0.1166	113	0.1168
			300	0.1152
w	2.214	0.1214	212	0.1208
w	2.174	0.1255	-	-
m	1.976	0.1518	104	0.1521
mw	1.803	0.1822	-	-
m	1.706	0.2037	312	0.2011
m	1.563	0.2425	402	0.2395
m	1.476	0.2720	410	0.2687
		0.3033	314	0.3056
w	1.336	0.3321	-	-
w	1.306	0.3477	413	0.3471
vw	1.280	0.3615	420	0.3584

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
w	1.226	0.3945	-	-
m	1.185	0.4225	405	0.4221

Crystal Symmetry : Rhombohedral⁵²

Lattice constants : $a = 5.31\text{Å}$, $\alpha = 95.5^\circ$.

X-ray data for Na₂ReF₆.Fe-K α_1 radiation.

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
s	5.091	0.0363	011	0.372
			002	0.372
vs	4.526	0.0457	100	0.0464
s	3.548	0.0743	110	0.0743
ms	2.922	0.1098	112	0.1115
			020	0.1116
			013	0.1116
s	2.804	0.1194	021	0.1209
mw	2.520	0.1475	004	0.1488
			022	0.1488
mw	2.449	0.1562	120	0.1580
			113	0.1580
w	2.313	0.1749	014	0.1767
mw	2.248	0.1856	200	0.1856
m	2.192	0.1949	201	0.1949
			122	0.1952
			104	0.1952
			023	0.1953
vs	1.870	0.2678	203	0.2693

<u>Intensity</u>	<u>$d(\text{\AA})$</u>	<u>$\sin^2\theta(\text{obs.})$</u>	<u>(h,k,l)</u>	<u>$\sin^2\theta(\text{calc.})$</u>
m	1.777	0.2964	220	0.2972
			213	0.2972
			130	0.2975
m	1.687	0.3293	222	0.3344
m	1.676	0.3337	204	0.3344
w	1.650	0.3438	025	0.3441
vw	1.635	0.3498	—	—
mw	1.587	0.3720	—	—
m	1.524	0.4032	—	—
w	1.515	0.4077	116	0.4091
e	1.501	0.4152	300	0.4176
mw	1.452	0.4440	310	0.4455
mw	1.399	0.4778	—	—
mw	1.390	0.4843	042	0.4836
			035	0.4836
			017	0.4836
mw	1.377	0.4932	140	0.4928
			126	0.4928
m	1.345	0.5177	—	—
ms	1.287	0.5646	322	0.5664
			304	0.5664

<u>Intensity</u>	<u>d(Å)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
w	1.266	0.5843	234	0.5855
w	1.254	0.5949	008	0.5942
			044	0.5942
m	1.223	0.6263	-	-
m	1.216	0.6330	136	0.6323
w	1.208	0.6415	241	0.6413
			207	0.6413
			144	0.6416
			108	0.6416
mw	1.192	0.6586	-	-
mw	1.184	0.6689	330	0.6687
			242	0.6692
			235	0.6692
			217	0.6692
ms	1.161	0.6952	050	0.6975
ms	1.146	0.7127	-	-
w	1.131	0.7326	052	0.7347
mw	1.123	0.7432	400	0.7424
			150	0.7439
ms	1.098	0.7778	411	0.7796
			402	0.7796
w	1.072	0.8153	334	0.8175

<u>Intensity</u>	<u>d(A°)</u>	<u>sin²θ(obs.)</u>	<u>(h,k,l)</u>	<u>sin²θ(calc.)</u>
mw	1.044	0.8605	-	-
mw	1.031	0.8817	250	0.8831
		0.8899	422	0.8912
			404	0.8912
s	1.010	0.9254	-	-
w	0.9990	0.9390	209	0.9389
m	0.9901	0.9558	01,10	0.9579

Crystal Symmetry : Orthorhombic

Lattice constants : a = 5.03A° ; b = 5.81A° ; c = 10.1A° .

C H A P T E R I I I

MIXED HALOBORATE ANIONS.

Triphenylhalomethanes react with boron halides to give coloured adducts $\text{Ph}_3\text{CX} \cdot \text{BY}_3$ ^{68, 69, 70} which might be expected to contain BXY_3^- anions (where X or Y = F or Cl). Binary mixtures of boron halides equilibrate to form mixtures of all possible halides but rapid disproportionation to the symmetrical boron halide compounds prevents isolation of the mixed species.^{71, 72} Similar disproportionation might be expected to occur during the formation of the mixed anions but a study of the infrared spectra of the adducts $\text{Me}_4\text{NCl} \cdot \text{BF}_3$, $\text{Et}_4\text{NCl} \cdot \text{BF}_3$, $\text{NOCl} \cdot \text{BF}_3$, $\text{PH}_4\text{Cl} \cdot \text{BF}_3$ and $\text{PCl}_5 \cdot \text{BF}_3$ has been taken to show that the compounds contain the BF_3Cl^- anion.^{73, 74}

The BF_3Cl^- group has the C_{3v} symmetry with six fundamental modes of vibration all active in the infrared.⁷⁵ The anion is isoelectronic with chlorotrifluoromethane whose infrared spectrum has been examined by Thompson and Temple⁷⁶ and Waddington⁷⁴ and Klanberg have assigned the bands in the spectrum of the BF_3Cl^- ion by comparison with CF_3Cl . (Table VII).

Table VII.The infrared spectrum of the BF_3Cl group.

$\text{POl}_4\text{BF}_3\text{Cl}$	$\text{PH}_4\text{BF}_3\text{Cl}$	NOBF_3Cl	$\text{Me}_4\text{NBF}_3\text{Cl}$	CF_3Cl	Assignment
466			456	478	sym.X-F def. V_3 (A_1)
556		522	520		
		533	544	561	asym.X-F def. V_5 (E)
650		645	645	783	X-Cl stretch V_2 (A_1)
		765	767		V_6 (E) + V_2 (A_1)
844			854	1092	
880			887	1102	sym.X-F stretch V_1 (A_1)
				1112	
	1028	1028	1037	1210	asym.X-F stretch V_4 (E)
	1063	1077	1071	1265	
1200	1195	1194	1198		V_2 (A_1) + V_5 (E)

Infrared spectra of the adducts $\text{Ph}_3\text{CX} \cdot \text{BY}_3$.

It is generally accepted that the carbonium ion is stabilised by resonance between canonical forms in which the positive charge is located either on the central carbon atom or alternatively on the ortho and the para carbon atoms in the benzene ring.⁷⁷ As in the triphenylmethyl radical^{78, 79} this type of resonance stabilisation is expected to be greatest for an all planar configuration of the ion (symmetry class D_{3h}). However, such a configuration⁸⁰ would give rise to great steric hindrance between the ortho hydrogens of adjacent benzene rings. It is therefore much more probable that the structure is distorted out of the plane by rotation of one or more benzene rings about the central bonds, the valence bonds to the central atom remaining coplanar. This rotation would then relieve the steric strains in the molecule but would not necessarily inhibit conjugation between the separate benzene rings. The relative insensitivity of the ultraviolet spectrum of this type of ion to the presence of bulky ortho substituents on the benzene rings⁸¹ also supports the idea that the triphenylmethyl cation itself is not planar.

The most symmetrical structure of this type is propeller like in shape with symmetry D_3 ; ⁸⁷ in this case, each benzene ring is rotated from the coplanar position in the same sense about a central C-C bond so as to relieve the steric strain. The existence of isomers of the cation of crystal violet [$4:4':4''$ tri(dimethylamino)triphenylmethyl chloride] has been explained ⁸⁰ in terms of this structure and a variant in which one benzene ring is rotated out of the original plane in the opposite direction to the others.

In the studies of the ultraviolet spectra of the triphenylmethyl cation and related ions ^{81,82,83} an unsymmetrical configuration of the parent ion is preferred. However, a study of the infrared spectrum of a series of salts which contain the triphenylmethyl cation has led Sharp and Sheppard ⁸⁷ to the conclusion that the cation has a propeller like (D_3) configuration rather than an all planar (D_{3h}) or an unsymmetrical structure. The nuclear magnetic resonance spectra ⁸⁴ of the triphenylmethyl cation and several of its derivatives substituted with methyl, methoxyl, and tert-butyl groups in the meta or para position agrees with this D_3 configuration. In no cases were

multiple substituent proton peaks observed. This is expected for the symmetrical propellor form but is also consistent with the one-ring-conjugated form if one assumes that the interconversion of isomers is too rapid to be detected by N.M.R. However, no splitting of the substituent proton resonances of the tri-p-anisylmethyl and tri-p-tolylmethyl cations was observed when the solutions were cooled to -80° .

In the present work the compounds $\text{Ph}_3\text{CCl} \cdot \text{BF}_3$, $\text{Ph}_3\text{CF} \cdot \text{BCl}_3$ and $\text{Ph}_3\text{CCl} \cdot \text{BCl}_3$ have been shown to possess the triphenylmethyl cation by comparison of their spectra with $\text{Ph}_3\text{C} \cdot \text{BF}_3$ and $\text{Ph}_3\text{C} \cdot \text{SnCl}_5$.⁶⁷ The trityl cation has characteristic bands at 1580, 1360 and 1300 cm^{-1} and these absorptions occur in the spectra of the adducts $\text{Ph}_3\text{CX} \cdot \text{BY}_3$.

The bands due to the groups BF_3Cl^- and BCl_3F^- could not be detected in the infrared as the cation spectra was very complicated and masked any bands that might be present in the anions. The BCl_4^- anion has bands⁶⁸ at 1449m, 1382m, 1265m, 699s and 664s (all in cm^{-1}) and in the spectrum of $\text{Ph}_3\text{C} \cdot \text{BCl}_4$ a strong band at 662 characteristic of the BCl_4^- group was detected. The other sharp band at 700 cm^{-1} was masked by a strong absorption at 700 cm^{-1} due to the trityl

cation. Thus the adduct $\text{Ph}_3\text{CCl} \cdot \text{BCl}_3$ may be formulated as $\text{Ph}_3\text{C}^+\text{BCl}_4^-$ but it is impossible on the present infrared evidence to be sure that the adducts $\text{Ph}_3\text{CCl} \cdot \text{BF}_3$ and $\text{Ph}_3\text{CF} \cdot \text{BCl}_3$ contain BF_3Cl^- and BCl_3F^- anions rather than the BF_4^- and BCl_4^- ions which would be expected if there were disproportionation upon crystallisation.

The BCl_4^- ion, like the isoelectronic carbon tetrachloride molecule, should be tetrahedral and have only two fundamental vibration frequencies active in the infrared, ν_3 and ν_4 . By comparison with the infrared spectrum of carbon tetrachloride⁷⁵ ($\nu_4 = 305 \text{ cm}^{-1}$) Waddington and Klanberg⁷⁴ have concluded that only one of these ν_3 , will be expected to be active above 400 cm^{-1} . In fact, two peaks are observed^{74, 85} in the infrared. There are two possible explanations of this splitting. It may be due to two isotopic species $\text{B}^{10}\text{Cl}_4^-$ and $\text{B}^{11}\text{Cl}_4^-$, or it may be due to the interaction by Fermi resonance of the combination $\nu_1 + \nu_4$, which has the same symmetry as ν_3 , with ν_3 , as a result of which it is shifted and gains in intensity. It is suggested that the latter explanation is correct for two reasons:⁷⁴ first the splitting is larger than one would expect for the two isotopic species and, secondly, a similar splitting is observed in carbon tetrachloride (ν_3 , $\nu_1 + \nu_4$;

797, 768 cm^{-1}). Thus the strong peaks at 699 and 664 in the BCl_4^- spectrum are V_3 and $V_1 + V_4$.

The BF_4^- group has characteristic bands⁸⁰ at 1032, 1058, 772, 535 and 521 cm^{-1} . In the spectrum of $\text{Ph}_3\text{C}^+\text{BF}_4^-$ these broad bands are difficult to locate especially when they are superimposed on the background spectrum, but a band at 520 cm^{-1} was observed together with a broad one between 1015-1027 cm^{-1} .

Nuclear magnetic resonance spectra.

The adducts $\text{Ph}_3\text{CX} \cdot \text{BY}_3$ are all soluble in dichloromethane to give yellow solutions which contain the triphenylmethyl carbonium ion. The F^{19} and B^{11} nuclear magnetic resonance spectra of a solution of trityl fluoroborate in dichloromethane at room temperature are single lines with no fine structure. The F^{19} spectrum of the tetrahedral BF_4^- ion should consist of a large quadruplet due to coupling with the B^{11} nucleus ($I = \frac{3}{2}$, relative abundance 81.2%) and a much smaller septet due to coupling with the B^{10} nucleus ($I = 3$, abundance 18.8%). The B^{11} spectrum should similarly show a quintet due to coupling with the F^{19} nuclei.

That boron-fluorine spin coupling in either F^{19} or B^{11} spectra was not observed with $Ph_3C.BF_4$ in dichloromethane could be due to a number of causes: (1) Quadrupole broadening of the B^{11} nuclei prevented observations; (2) there was interionic exchange of fluorine atoms; (3) the resolution was not high enough and the compound was not soluble to a sufficient extent. Cause (1) is immediately ruled out since fine structure of the expected form is in fact observed for the F^{19} spectrum of BF_3 and some derivatives containing B-F bonds.⁸⁷ Reason (2) and also (1) again is unlikely since $B^{11}-F^{19}$ splitting has recently been observed in an aqueous solution of sodium fluoborate. It is reported variously as 4.2 ± 0.3 c/s⁸⁸ and 2.0 ± 0.2 c/s.⁸⁹ Thus reason (3) is the most likely cause of the present inability to observe fine structure.

On mixing methylene chloride solutions of triphenylmethyl tetrafluoroborate and tetrachloroborate there is an immediate evolution of heat and the nuclear magnetic resonance spectrum (F^{19} or B^{11}) of the solution shows a single peak. The position of this peak varies in a systematic manner (see figures 1 and 2) with the relative amount of tetrafluoroborate and tetrachloroborate which

Figure 1.

Triphenylmethyl tetrahaloborates : F^{19} spectra.

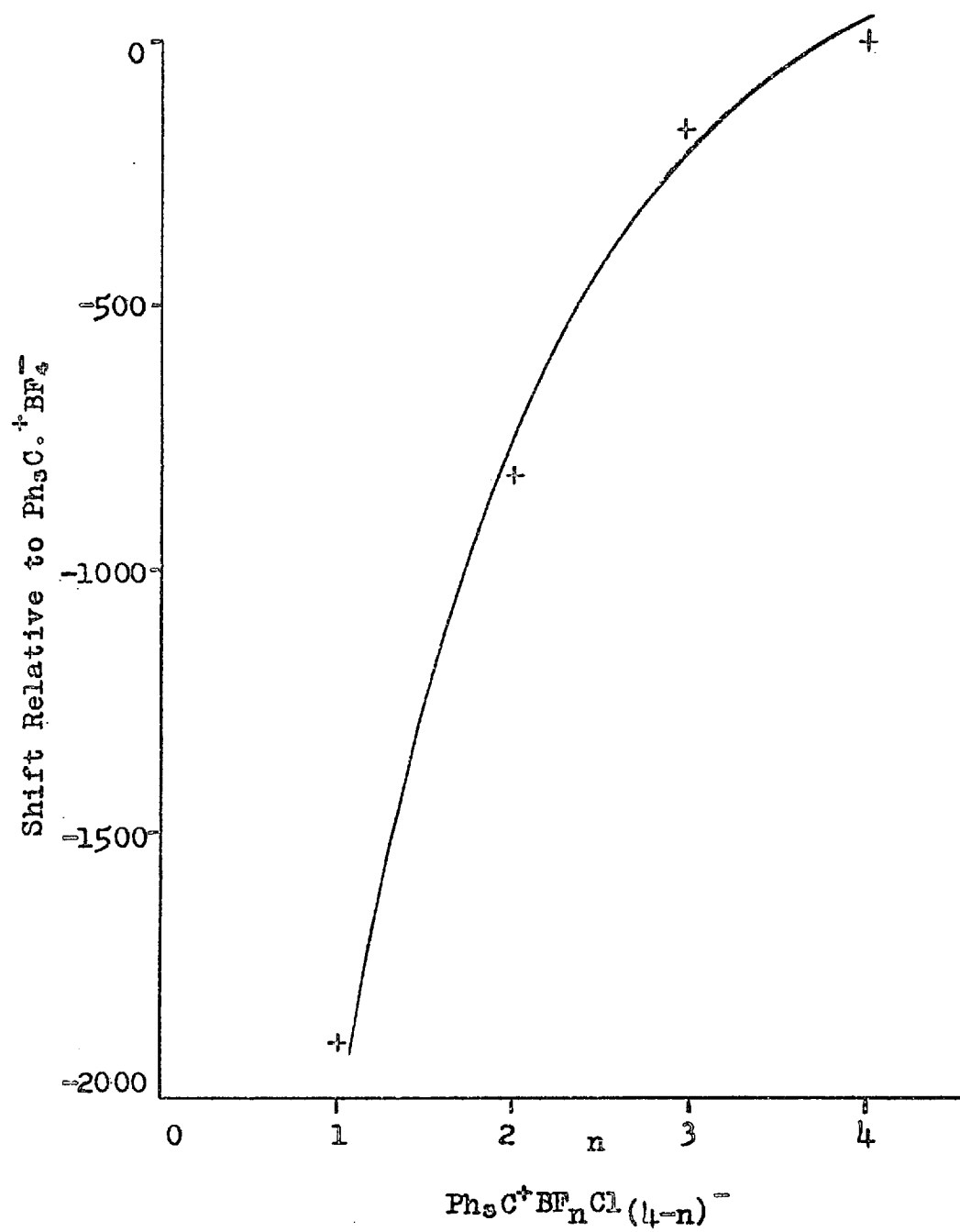
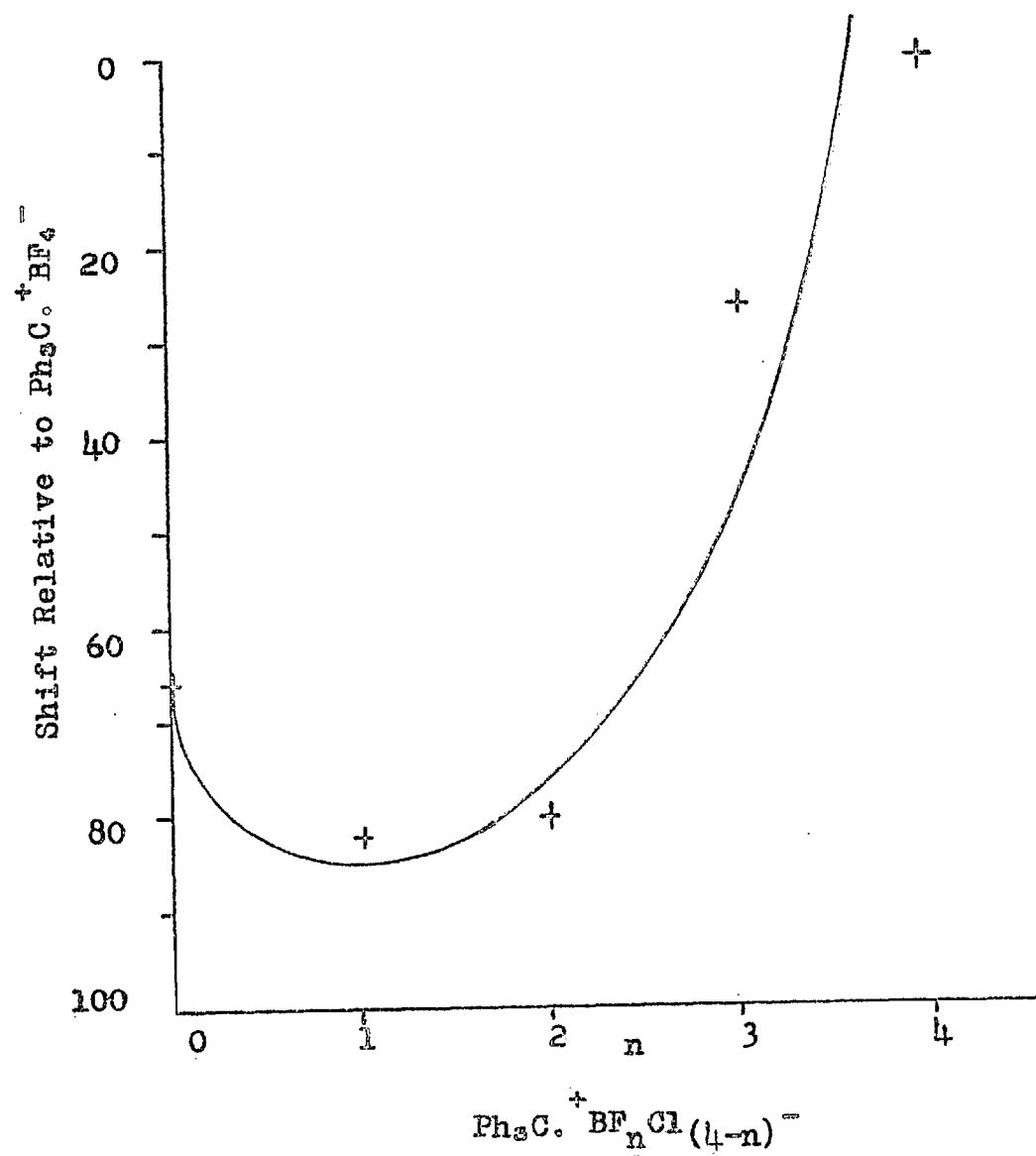


Figure 2.

Triphenylmethyl tetrahaloborates : B¹¹ Spectra.



have been mixed and it is inferred that there is rapid halogen exchange between the BF_4^- and BCl_4^- ions. Once again it is not possible to detect fine structure in the nuclear magnetic resonance bands of the mixed solutions. This could be due to the fact that splitting of the F^{19} resonance by the B^{11} was too small to be observed under the present conditions of relative insolubility or, more likely in view of the rapid reaction between tetrafluoroborate and tetrachloroborate anions, that the solutions contain discrete BF_6^- and BCl_4^- ions which are undergoing rapid exchange through a series of mixed haloborate anions. The B^{11} nuclear magnetic resonance spectra of solutions of the adducts $\text{Ph}_3\text{CCl} \cdot \text{BF}_3$ and $\text{Ph}_3\text{CF} \cdot \text{BCl}_3$ show single peaks at positions which correspond to the relative amounts of fluorine and chlorine implied by the empirical formulae but it is impossible to use the spectra as positive evidence for the presence of discrete BFCl_3^- and BF_3Cl^- ions in solution as there may be rapid exchange between other haloborate species to give the same result.

Shielding of the F^{19} and B^{11} nuclei.

The shielding of the F^{19} nuclei in the $\text{BF}_{(4-n)}\text{Cl}_n^-$ series increases with an increase in the amount of fluorine

present which is unexpected since replacement of chlorine by the more electronegative fluorine should decrease the electron density at the extra fluorines. However, a similar tendency has been observed in the F^{19} spectra of the isoelectronic chlorofluoromethanes⁸⁸ and the mixed boron halides.⁸⁷ In the boron halides these shifts have previously been explained in terms of multiple bonding between the boron and the fluorine (diagram 2).

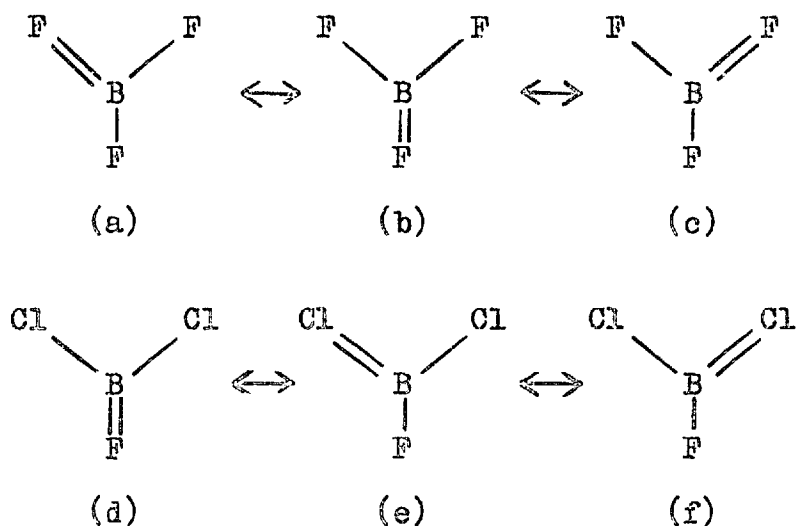


Diagram 2.

The marked shortening of the boron-fluorine bond distance observed in boron trifluoride led Pauling⁹⁰ to suggest that the resonance structures (a), (b) and (c) must contribute strongly to boron trifluoride. The ability to form double bonds appears to decrease sharply in the heavier elements and therefore resonance of this kind should be less important in boron trichloride and still smaller importance in boron tribromide. It must be assumed that these resonance interactions are sufficiently large so as to reverse the trend expected from the relative inductive effects of the different halogens. In the compound BFCl_2 the contribution of the hybrid (d) must be greater than (e) and (f) and this will explain the decreased shielding of the fluorine in the mixed fluoro-chloroboranes. This ability to form double bonds also explains why the Lewis acid strength of the boron halides increases in the series $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3 < \text{BI}_3$ ⁹¹ which is also unexpected from electronegativity concepts.

There is no possibility of back bonding in the BF_4^- ⁹² anion. However, to explain the increased length of the boron fluorine bond in going from boron trifluoride to the tetrafluoroborate ion the resonance shown in diagram 3 has been postulated.⁹³ Here the bond is being lengthened by

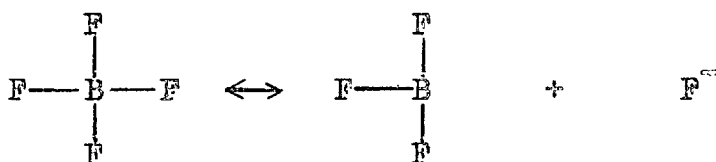


Diagram 3

the increased tendency for the electrons to be drawn towards the fluorine. In the mixed chloro-fluoroborates this resonance can also occur (diagram 4).

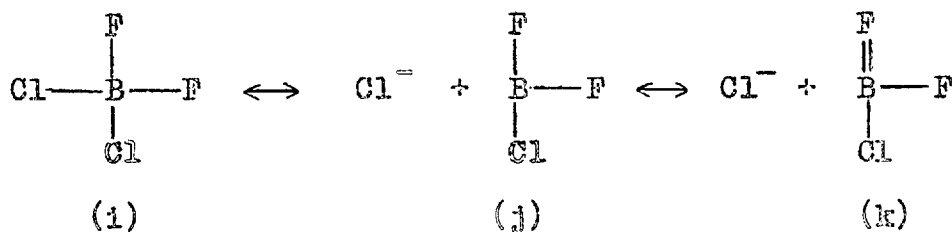


Diagram 4

In (j) multiple bonding can now occur and structures such as (k) will be more important where multiple bonding will preferentially occur between boron and fluorine. Thus as in the mixed boron halides the fluorine will become less shielded.

An X-ray analysis of the compound $\text{KF} \cdot 2\text{AlEt}_3$ has confirmed that it has the ionic structure $\text{K}^+[\text{Et}_3\text{Al}-\text{F}-\text{AlEt}_3]^-$,²⁴

and definite evidence has been obtained for the colinearity among Al-F-Al atoms. The Al-F distance ($1.80 \pm 0.6^\circ$) is close to that observed in Na_3AlF_6 ⁹⁵ which clearly indicates that Al and F atoms are bonded together. This data is in contrast to the fact that usual bridge bond distances are somewhat longer than the corresponding single bond distances.⁹⁵⁻⁹⁷ To account for this shortening it is supposed that there is partial sp hybridisation for the Al-F bond so that a partial π -bond character on the Al-F bond may arise from a certain overlap between the $2p_y$ and $2p_z$ filled fluorine orbitals and the 3d empty aluminium orbitals. Thus it does appear that fluorine can form partial π -bonds in some molecules.

The boron in the BF_4^- ion is more shielded than that in the BCl_4^- ion which is in agreement with previous observations,¹⁰³ presumably because once again double bonding which tends to increase the electron density at the central atom is more important in the former case.

Mechanism of the exchange between tetrafluoroborate and tetrachloroborate.

Various experiments have been carried out in attempts to obtain more information about the mechanism of halogen exchange between the BF_4^- and BCl_4^- anions. No ionic

fluorides are known which are soluble in methylene chloride or other organic solvents. Triphenylfluoromethane is covalent in the solid state⁶⁷ and a solution in methylene chloride when mixed with a solution of triphenylmethyl fluoroborate shows two peaks in the P^{19} nuclear magnetic resonance spectrum; one of these peaks is in the same position as in a solution of triphenylmethyl fluoroborate alone and originates from the fluoroborate ion. The other due to the covalent fluoride was quite sharp and distinct from it. This does not infer that exchange between fluoride ion and fluoroborate is non-existent as presumably there will only be a tiny amount of ionic fluoride present and any exchange that might take place would not be observed as the concentrations would be too small. However, a study of the $B^{11}-P^{19}$ splitting of the fluoroborate ion in aqueous solution in the presence of fluoride ion⁶⁸ indicates an absence of fast exchange between fluoride ions and fluoroborate in that solvent. The hydrolysis of the tetrafluoroborate ion to the hydroxy trifluoroborate ion is also slow.⁶⁹ This hydrolysis probably proceeds by way of separation of an F^- ion from a BF_4^- anion and these results are in favour of a very slow rate for this separation. A solution of triphenylchloromethane in methylene chloride is yellow and

hence contains a quantity (unknown) of chloride ions; a mixture of such a solution and a solution of triphenylmethyl fluoroborate shows a single F^{19} nuclear magnetic resonance absorption in the normal position for the fluoroborate ion. The position of this line is steady and remains unchanged over a period of two hours. Simple chemical tests show that boron trichloride reacts with triphenylmethyl fluoroborate in methylene chloride solution to give a product containing both chlorine and fluorine. Boron trichloride and tribromide both react with crystalline sodium fluoroborate to give mixed haloborates. The results appear to indicate a lack of reaction between fluoroborate and halide ions but rapid reaction between fluoroborate anions and boron trihalides and whilst it is impossible to discuss reaction mechanisms with any certainty in the absence of rate data, it would appear that a mechanism in which a tetrachloroborate ion dissociates to boron trichloride and chloride ion with subsequent attack of the boron trichloride upon tetrafluoroborate ions would be in agreement with the present observations on the reaction between chloroborate and fluoroborate ions.

EXPERIMENTAL

Preparation of triphenylchloromethane.

Ordinary reagent grade triphenylchloromethane recrystallised from dry benzene was used.

Preparation of triphenylfluoromethane.

Triphenylfluoromethane was prepared from triphenylchloromethane and anhydrous hydrogen fluoride.¹⁰⁰ The triphenylchloromethane was placed in a polythene bottle fitted with an inlet and outlet tube and anhydrous hydrogen fluoride was condensed onto the chloride (diagram 5).

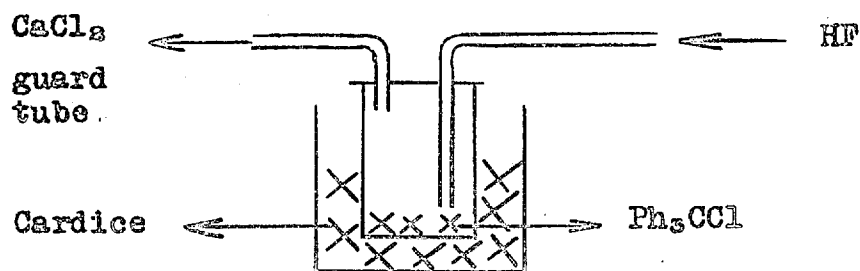


Diagram 5.

When sufficient hydrogen fluoride had condensed it was evaporated in a stream of dry nitrogen. The solid left was recrystallised twice from 30-40° petroleum ether and a white crystalline solid was obtained m.p. 101° (lit. 102-104°).

Preparation of silver fluoroborate.

Silver fluoroborate was prepared by addition of bromine trifluoride to a suspension of silver borate in bromine.¹⁰¹ Excess bromine and bromine trifluoride were removed under vacuum and the product was heated for one hour at 150° under vacuum.

Preparation of boron trifluoride.

Boron trifluoride was used from a cylinder which was kindly supplied by the Imperial Smelting Corporation and was dried and purified by passage through a suspension of boric oxide in concentrated sulphuric acid.

Preparation of boron trichloride.

A commercial sample of boron trichloride was used. Hydrogen chloride was removed by distillation under vacuum.

Preparation of boron tribromide.

Boron tribromide was prepared by heating a mixture of aluminium bromide and potassium fluoroborate.¹⁰² The temperature of the reaction flask was gradually raised from 150° to 175° over a period of 4 hours and the product was condensed in liquid oxygen. Hydrogen bromide was removed from the boron tribromide by distillation and bromine was removed by shaking with mercury.

Preparation of triphenylmethyl fluoroborate.

Triphenylmethyl fluoroborate was prepared from ether solutions of trityl chloride and silver fluoroborate in the dry box.⁶⁷ The carbonium salt and silver chloride were filtered and dried under vacuum. The trityl fluoroborate was also prepared by condensing boron trifluoride on to a solution of trityl fluoride in sodium dried toluene. The reactants were allowed to warm to -80° and after 30 minutes excess boron trifluoride and toluene were removed under vacuum.

Preparation of triphenylmethyl chlorotrifluoroborate.

$\text{Ph}_3\text{C}.\text{BF}_3\text{Cl}$ was prepared by condensing boron trifluoride on to a solution of trityl chloride in dry toluene. The reactants were allowed to warm to -80° and after 30 minutes excess boron trifluoride and toluene were removed under vacuum. Found for triphenylmethyl trifluorochloroborate: Cl, 11.0. Calc. for $\text{Ph}_3\text{C}.\text{BF}_3\text{Cl}$, 10.2%.

Preparation of triphenylmethyl fluorotrichloroborate.

$\text{Ph}_3\text{C}.\text{FBCl}_3$ was prepared by condensing boron trichloride on to a solution of trityl chloride in sodium dried toluene. The reactants were allowed to warm to room temperature and after 30 minutes excess boron trichloride and toluene were

removed under vacuum. Found for triphenylmethyl fluoro-trichloroborate: Cl, 33.2. Calc. for $\text{Ph}_3\text{C}.\text{BCl}_3\text{F}$, Cl, 28.0%.

At low temperatures (about -180°) the reaction of boron trichloride on trityl fluoride produced a deep red compound. However, as the reactants reached room temperature the red complex quickly changed to the yellow carbonium salt. A similar reaction was observed with trityl chloride and boron trichloride.

Preparation of triphenylmethyl tetrachloroborate.

$\text{Ph}_3\text{C}.\text{BCl}_4$ was prepared from the reaction between boron trichloride and trityl chloride in sodium dried toluene as described for triphenylmethyl fluoro-trichloroborate.

Found for triphenylmethyl tetrachloroborate: Cl, 35.4.

Calc. for $\text{Ph}_3\text{C}.\text{BCl}_4$, 35.8%.

Reaction of boron trichloride and tribromide with fluoroborates.

Boron trichloride was condensed on to a solution of triphenylmethyl tetrafluoroborate in dry dichloromethane. The reactants were allowed to warm to room temperature and after 20 minutes the excess boron trichloride and solvent were removed under vacuum. Found for the residue: Cl, 28.5%. This analysis corresponds closely to that required for $\text{Ph}_3\text{C}.\text{BFCl}_3$ and it is apparent that the excess chlorine found in

the product from the reaction Ph_3CF plus BCl_3 results from displacement of some of the fluorine as boron trifluoride by the boron trichloride. Boron trichloride and boron tribromide in excess were reacted with sodium fluoroborate (recrystallised from water and dried in vacuum at 120°) in a Carius tube over a period of about two days. Found for the reaction involving boron trichloride: Cl, 6.3%.

Found for the reaction involving boron tribromide: Br, 27.1%.

Infrared spectra.

Infrared spectra were recorded in nujol and hexachlorobutadiene mulls prepared in the dry box. Spectra were recorded as follows (figures in cm.^{-1}).

$\text{Ph}_3\text{C}.\text{SnCl}_4$.⁶⁷ 3040w, 2920w, 1577s, 1482s, 1447s, 1406w, sh., 1358s, 1293s, 1185m, 1166w, 1117s, 1105s, 1088s, 1063s, 1036w, 1031w, 1011m, 996m, 981m, 951w, 915w, 844s, 807s, 768s, 699s, 688w, sh., 668w, sh., 658w, 622s, 609s, 470m, 463m.

$\text{Ph}_3\text{C}.\text{BF}_4$.⁶⁷ 3080w, 2910w, 2850w, 1587s, 1565w, sh., 1490s, 1454s, 1364m, 1313w, 1299s, 1195w, 1172w, 1117s, 1105s, 1090s, 1038m, 1015-1027m, broad,⁸⁸ 995w, 983w, 953w, 917m, 847w, sh., 833s, 809s, 782w, sh., 700s, 670w, sh., 658w, 622s, 611s, 520s,⁸⁸ 470s.

⁸⁸ Anion spectra. KBF_4 ⁸⁸ 1058, 1032, 534, 521.

KBCl_4 ⁸⁸ 1449, 1382, 1265, 699, 664.

Ph₃C.BF₃Cl. 2930w, 1575s, 1490s, 1450s, 1360m, 1295s, 1192w, 1170w, 1116s, 1103s, 1080w, 1067w, 1058w, 1052w, 1028w, 1017w, 1010w, 1005w, sh., 996w, sh., 928m, 889m, 843m, 818w, 805w, 753s, 740s, 693s, 661w, 622s, 614w, sh., 500w..

Ph₃C.BFCl₂. 2930w, 1577s, 1485s, 1448s, 1365w, 1300w, 1185m, 1166w, 1118s, 1102s, 1090s, 1063s, 1032w, 1008m, 998m, 979m, 950w, 916m, 895w, 838s, 805s, 768s, 738w, 727w, [695s, 858w, sh., 662s, broad], 622s, 609s, 462w.

Ph₃C.BCl₄. 2950w, 1580s, 1480s, 1451s, 1359s, 1297s, 1180m, 1117s, 1102s, 1095s, 1063s, 1041w, 1012m, 998s, 978s, 949m, 916m, 838s, 804s, 767s, 726w, [700s, 662s, broad][⊗], 621s, 608s, 462m.

Nuclear magnetic resonance.

The boron and fluorine resonances of the tetrafluoroborate ion were used as standards and signals were referenced by replacement, all measurements were made at $21 \pm 1^\circ$. The results for the mixed solutions containing tetrafluoroborate and tetrachloroborate are shown graphically in figures (1) and (2) (pages 113, 114). The principle uncertainty

[⊗] Anion spectra. KBF₄ ^{ss} 1058, 1032, 534, 521.
 KBCl₄ ^{ss} 1449, 1382, 1265, 699, 664.

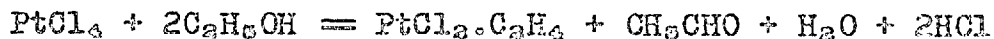
in these results arises in the measurement of concentrations since it is difficult to make precise measurements on such moisture-sensitive materials. The presence of triphenylmethyl carbinol does not influence the position of the tetrafluoroborate or other signals. Nuclear magnetic resonance shifts recorded were (p.p.m.) $\text{Ph}_3\text{C}.\text{BF}_4$, 0; $\text{Ph}_3\text{C}.\text{BClF}_3$, -26; $\text{Ph}_3\text{C}.\text{BCl}_2\text{F}$, -72; $\text{Ph}_3\text{C}.\text{BCl}_4$, -66; 1:1 mixture of $\text{Ph}_3\text{C}.\text{BF}_3\text{Cl}$ plus $\text{Ph}_3\text{C}.\text{BClF}_3$, -80; 1:1 mixture of $\text{Ph}_3\text{C}.\text{BF}_4$ plus $\text{Ph}_3\text{C}.\text{BCl}_4$, -80.

CHAPTER IV

OLEFINE-PLATINUM-FLUORIDE COMPLEXES.

Although olefine-platinum-halide complexes are well known for chlorides, bromides and iodides,^{104,105} no complexes in which platinum or any other metal is bonded to both fluorine and olefine ligands are known.

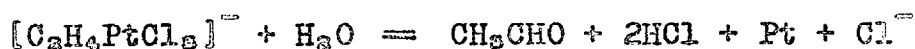
The first olefine-metal-halide complex was prepared by Zeise in 1827 who published a note¹⁰⁶ concerning his research on platinum compounds. Three years later this work was published in Latin¹⁰⁷ and the following year a condensed form appeared in German.¹⁰⁸ Zeise discovered that when platonic chloride was boiled with alcohol an acid solution resulted. By treating this solution with potassium chloride he obtained a compound whose composition was indicated by analysis to be $KCl.PtCl_2.C_2H_4$. Since an aldehyde was detected as one of the products of the reaction of an alcohol with platonic chloride. Birnbaum¹⁰⁹ proposed the following equation as the probable course of the reaction:



Zeise¹¹⁰ had also demonstrated the presence of an aldehyde in his distillate. Moreover, he had isolated ethyl chloride,

which was formed as a secondary product and literally expressed the above equation in words.

Anderson¹¹¹ succeeded in isolating the compound $\text{PtCl}_2 \cdot \text{C}_2\text{H}_4$ from the solution obtained by reducing sodium chloroplatinate with alcohol and showed that the hydrolysis of Zeise's salt at 100° occurred as follows:



Much later Chatt¹¹² obtained the compound $\text{Pt}(\text{C}_2\text{H}_4)_2\text{Cl}_2$ by reaction of ethylene with $\text{Pt}(\text{C}_2\text{H}_4)\text{Cl}_2$ in acetone at -80° .

The complexes $\text{KCl} \cdot \text{PtCl}_2 \cdot \text{C}_2\text{H}_4$ and $\text{PtCl}_2 \cdot \text{C}_2\text{H}_4$ are now formulated as $\text{K}[\text{C}_2\text{H}_4\text{PtCl}_5]^{113}$ and $[\text{C}_2\text{H}_4\text{PtCl}_2]_2$ where in the latter compound the two platinum atoms are joined by chlorine bridges.¹¹⁴

Dewar¹¹⁵ has explained the bonding in silver(I) olefine complexes by means of a σ -bond formed by overlap of a vacant 5s orbital on the silver with a filled π -2p orbital of the olefine and a π -bond formed by overlap of a filled 4d orbital of the metal with a vacant π^*-2p antibonding orbital of the olefine (diagram 6).

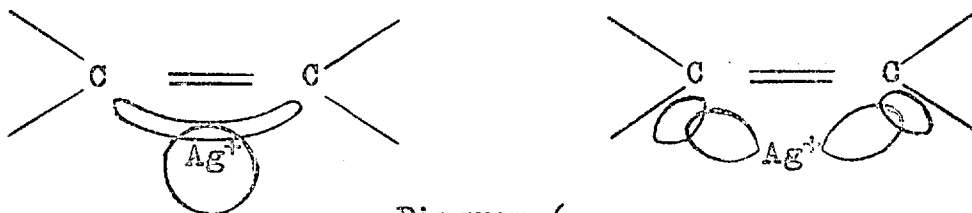


Diagram 6.

The extension of the Dewar concept to explain the bonding in olefine complexes of platinum(II) has been applied by Chatt,¹¹³ (diagram 7).

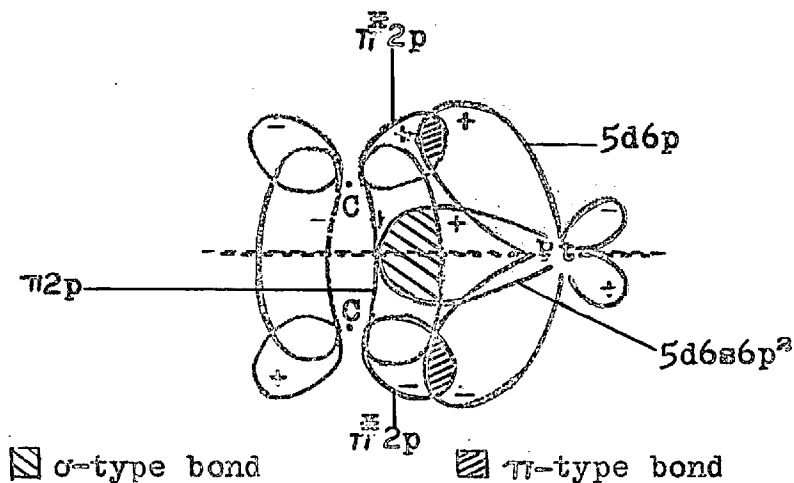


Diagram 7.

A σ -type bond is formed by overlap of a $5d6s6p^3$ hybrid orbital of the platinum atom with the π -orbital of the olefine, and a π -type bond is formed by overlap of a filled $5d$ orbital of the metal atom with the antibonding π -molecular orbital of the olefine. The π -type bond is strengthened by hybridisation of the $5d$ orbital of the platinum to give a dp hybrid which is more suitably shaped than the unhybridised $5d$ orbital to provide a large overlap with the orbitals of the olefine. It is clear that olefine-metal bonding is closely

similar in type to metal-carbon monoxide bonding in metal carbonyl derivatives and this undoubtedly explains the frequently noted resemblance in stoichiometry and chemical properties between olefine-metal halides and metal carbonyl halides especially of platinum(II) and palladium(II) (Table VIII).

Table VIII.

Platinum(II) and palladium(II) olefine and carbonyl halides.

Platinum	Palladium
$[\text{COPtCl}_3]_2^a$; $[\text{C}_2\text{H}_4\text{PtCl}_3]_2^c$	$[\text{COPdCl}_2]_2^e$; $[\text{C}_2\text{H}_4\text{PdCl}_3]_2^f$
$[(\text{CO})_3\text{PtCl}_3]^a$; $[(\text{C}_2\text{H}_4)_2\text{PtCl}_3]^d$	
$\text{M}^+[\text{COPtCl}_3]^-^b$; $\text{M}^+[\text{C}_2\text{H}_4\text{PtCl}_3]^-^c$	$\text{M}^+[\text{COPdCl}_3]^-^e$

^a Irving and Magnusson, J., 1956, 1860; ^b Zeiss, "Organometallic Chemistry", Reinhold, New York, 1960, p.511;

^c Chatt and Duncanson, J., 1953, 2939; ^d Chatt and Wilkins, ibid, 1952, 2622; ^e Irving and Magnusson, ibid, 1958, 2283;

^f Kharasch, Seyler and Mayo, J. Amer. Chem. Soc., 1938, 60, 882.

The existence of stable square planar olefine complexes of platinum(II), palladium(II) and rhodium(I) led Chatt and Venanzi^{11c} to suggest that the presence of a vacant p_z orbital

on the metal was necessary for the formation of olefine complexes, since this could form hybrid orbitals with the filled d_{xz} and d_{yz} orbitals suitable for forming strong π -bonds with the antibonding orbitals of the olefine. It was suggested that d-orbitals alone do not always give sufficiently good overlap, and that some p-character is always necessary. In agreement with this is the failure to isolate six-coordinate olefine complexes of platinum(IV) and rhodium(III) by halogen addition to the corresponding platinum(II) and rhodium(I) complexes.^{110,117} However, this criterion of p-character is not always valid since stable, six coordinate olefine complexes of ruthenium(II) have been isolated.^{117,118}

By analogy with the preparation of olefine-platinum-chloride complexes the ideal starting material for the preparation of the corresponding fluoride complexes would be sodium fluoroplatinite(II). However, no divalent complex fluoride of platinum is known and platinum difluoride has not been prepared although bistriphenylphosphine platinum difluoride is now known.¹¹⁹ All attempts to reduce the PtF_6^{3-} ion to the PtF_3^{3-} ion in aqueous media with sulphur dioxide, potassium oxalate, hydrazine,

hydroxylamine, stannous fluoride, sodium stannite, hydrogen, methanol or hydrogen peroxide have so far failed,¹¹⁰ and it is suggested from extrapolation of the standard potentials for the reduction of other complex halides of platinum(IV) that the fluoroplatinite ion is probably unstable with respect to disproportionation to platinum and the hexafluoroplatinate(IV) ion.

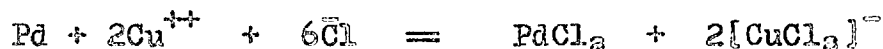
Reactions of olefines and acetylenes with aqueous solutions of sodium hexafluoroplatinate.

Reactions of olefines with aqueous solutions of sodium hexafluoroplatinate might lead to the required products. When a solution of sodium hexafluoroplatinate in water is shaken in an atmosphere of ethylene there is an immediate precipitation of hydrated platinic oxide and there is a strong odour of acetaldehyde. Passage of acetylene through an aqueous solution of sodium hexafluoroplatinate also causes precipitation of hydrated platinic oxide and other olefines induce hydrolysis in a similar manner. Thus cyclohexene gives cyclohexanone in a 10% yield based on the amount of sodium hexafluoroplatinate taken and propylene, 1-pentene, 2-pentene, 1-octene, 1-octyne, tetrafluoroethylene, hexafluoropropene and hexafluoro-2-butyne all give aldehydes or ketones. However, the yields are so small that it is not

possible to make positive identifications of the products, but with budadiene croton-aldehyde was identified as one of the products. In addition to the oxidation product cyclohexene also yields cyclohexyl fluoride presumably by direct addition of the hydrogen fluoride formed by hydrolysis of the fluoroplatinate. It has previously been observed that cyclohexene adds hydrogen fluoride at or below room temperature to yield cyclohexyl fluoride.¹³⁰ In these reactions there is some reduction to a platinum(II) species but this has not been identified. These results are very similar to those of Smidt¹³¹ on the oxidation of olefines in the presence of palladium(II) chloride. This oxidation with palladous chloride is a one step reaction and can be written as a simple equation.



On an industrial scale the palladium metal must be reconverted to palladous chloride and this can be done by catalysing the reaction with cupric chloride which oxidises the palladium metal back to palladous chloride.



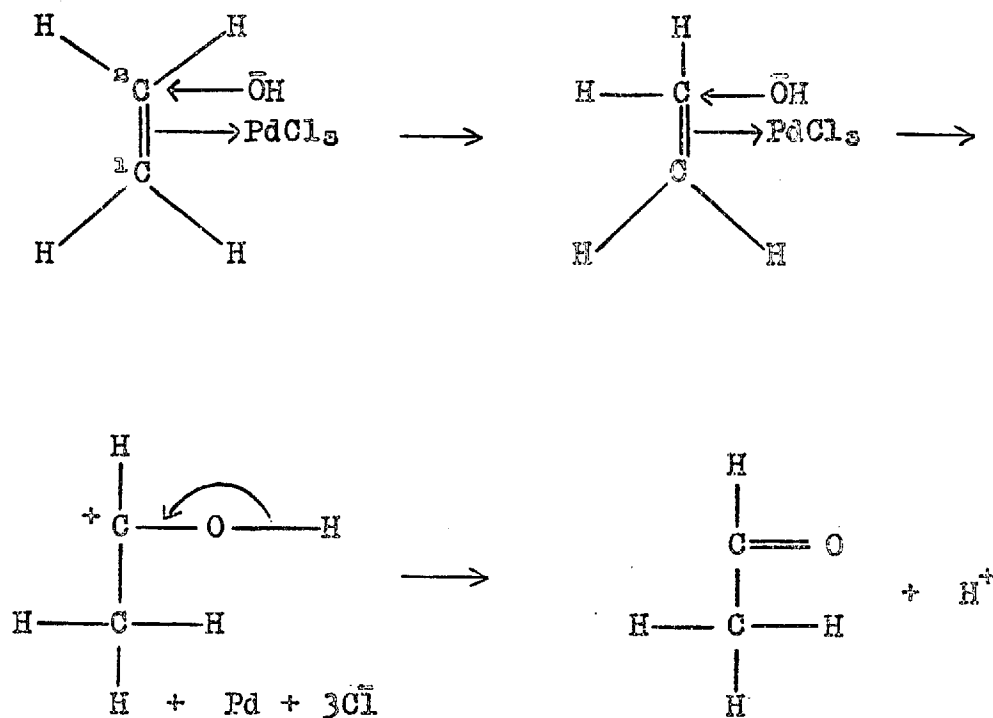
The cupric chloride is regenerated with oxygen.



The overall equation for the oxidation of the olefine is:



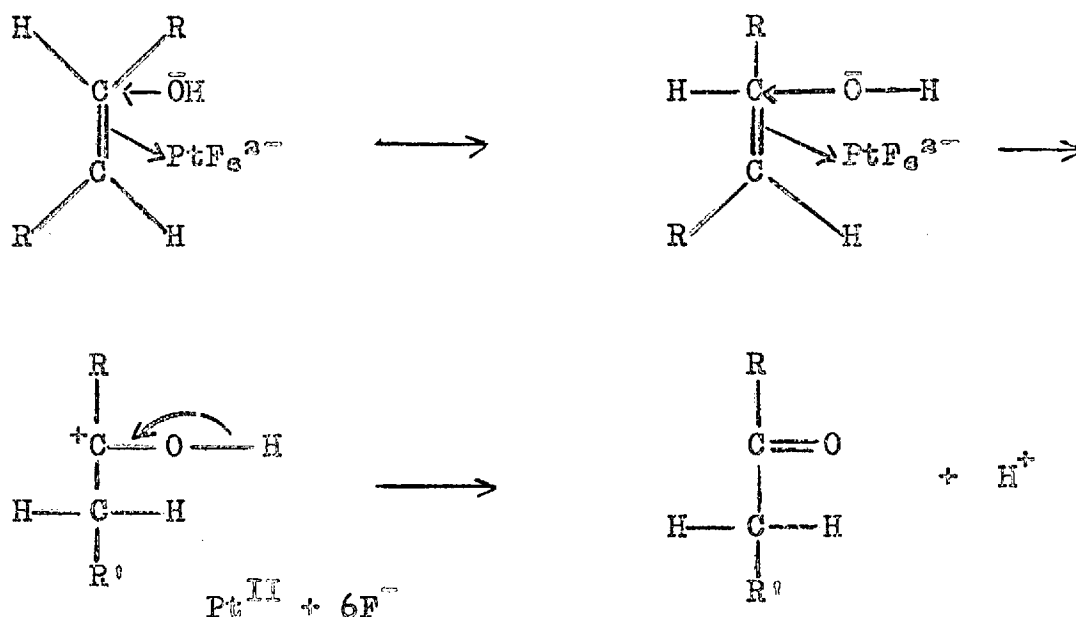
The following mechanism for the oxidation of the olefine which involves the formation of an olefine-palladium-chloride complex has been postulated.



The hydroxide ion attacks the olefine bound to the palladium provided that simultaneously a hydride ion from carbon atom 2 can migrate to carbon atom 1.

Although the reaction takes place in an acidic medium a formulation of the mechanism with a hydroxide ion as attacking agent is preferred because this explains the inhibiting reaction of protons without assuming another intermediate.

An analogous mechanism can be postulated for the oxidation of olefines with an aqueous solution of sodium hexafluoroplatinate if the initial formulation of an olefine-platinum-fluoride complex is envisaged.



The overall equation is:



and there is a final liberation of hydrofluoric acid.

In the present work it has been found that the hexafluoroplatinate ion is hydrolysed by alkali and the appearance of the hydrated platinic oxide is due to alkaline hydrolysis of the hexafluoroplatinate ion.

Reaction of cyclohexene with sodium hexafluoromanganate.

Since aqueous solutions of sodium hexafluoroplatinate give aldehydes or ketones with olefines or acetylenes other transition metal complex fluorides might be expected to have similar properties. A reaction of sodium hexafluoromanganate in 40% aqueous hydrogen fluoride with cyclohexene gave a ketone in such a small quantity that it could not be characterised. Presumably in this reaction most of the cyclohexene is polymerised by the hydrogen fluoride.¹²⁰

Reactions of olefines with sodium hexafluoroplatinate suspended in anhydrous solvents.

It would appear from the reactions of olefines with sodium hexafluoroplatinate that the existence of olefine-platinum-fluoride complexes is established but they will only be isolated from non-aqueous solvents. However, attempts to prepare these complexes in an anhydrous media were unsuccessful. Cyclohexene did not react with sodium

hexafluoroplatinate suspended in ether, tetrahydrofuran or diethyleneglycol-dimethyl ether (diglyme) and there was no apparent reaction between cycloocta-1:5-diene and sodium hexafluoroplatinate suspended in diglyme. The fluoro-platinate appeared to be slightly soluble in tetrahydrofuran and diglyme judging from the faint yellow colourations of the solutions and was even more soluble in propionic acid. It was, however, insoluble in vinyl acetate and ethyl acetate.

Reactions of olefines and acetylenes with platinic fluoride and palladium trifluoride.

Olefines react with platinic chloride or bromide suspended in warm glacial acetic acid to give olefine-platinum-chlorides or bromides.^{12a} However, cyclohexene and diphenyl-acetylene react with platinic fluoride suspended in benzene to give metallic platinum. Evidently the fluoride is too reactive and fluorinates the benzene and olefine, itself being reduced to platinum. A pressure of ethylene and tetrafluoroethylene also reduces the fluoride to platinum and with the latter compound teflon is produced. Similarly platinum is produced from the reaction of tetrafluoroethylene and platinic fluoride suspended in anhydrous hydrogen fluoride.

Hexafluorobut-2-yne reacts with platinum fluoride at room temperature to give a dark red solid which recrystallizes from acetone to give dark red crystals. The compound has strong carbon-fluorine bands in the infrared but lack of microanalytical facilities at present for the analysis of carbon-fluorine compounds has prevented any attempts at formulating the compound. Analyses for carbon and platinum have been obtained but these are not consistent. Reactions of a methanolic solution of palladous chloride with phenyl-ethyl-acetylene or phenyl-methyl-acetylene give cyclo-octatetraene derivatives of Pd(II).¹²⁸ Similar polymerisation may have occurred with the fluoroacetylene¹⁴¹ but other possibilities where the platinum-fluorine bond adds across the acetylene to give vinyl derivatives of the type $\text{PtF}_n(-\text{CCF}_3=\text{CFCF}_3)_{4-n}$ (where $n = 0, 1, 2$ or 3) are also possible.

The reaction of hexafluorobut-2-yne with palladium trifluoride gives a red oil and a black solid. The red oil is a polymer of the acetylene and has a molecular weight of about 5081. The colour is presumably due to conjugation in the polymer. Previous polymerisations of the acetylene have given hexakis(trifluoromethyl)benzene^{124, 125, 126} and very high molecular weight ($\approx 10,000$) polymers.¹²³

The black solid was soluble in acetone but was not so stable in solution as the platinum fluoroacetylene compound although it did have a similar infrared spectrum. Lack of analytical results prevents any formulation of this compound although it is probably similar to the platinum compound.

Reactions of olefines and acetylenes with bis(triphenylphosphine)platinum difluoride.

Bis(triphenylphosphine)platinum difluoride reacts with carbon monoxide to give $(\text{Ph}_3\text{P})_2\text{Pt}(\text{CO})_2\text{F}_2$.¹⁴ As triphenylphosphine exerts a strong trans effect in square planar platinum complexes^{127, 128} the phosphine-platinum-fluoride probably has a cis configuration and one would expect the carbonyls to be above and below the plane of the molecule in an octahedral configuration. Thus diolefines would not be expected to occupy the coordinating positions of the two carbonyl groups and it was observed that norbornadiene failed to react with the phosphine-platinum-fluoride in dichloromethane. Mono-olefines or acetylenes might be expected to react but no reaction was observed between the phosphine-platinum-fluoride and hexafluorobut-2-yne.

Tetrafluoroethylene reacts with bistriphenylphosphine platinum difluoride in anhydrous hydrogen fluoride at 150°

to give a very dark green solid. Tetrafluoroethylene reacts with mercuric fluoride in arsenic trifluoride to give bis(pentafluoroethyl mercury)¹²⁰ and fluoro-olefines add mercuric fluoride in anhydrous hydrogen fluoride to give perfluoroalkyl mercury derivatives.¹³⁰ Thus by analogy a similar reaction may have occurred with the platinum compound to give $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{F}_5)_2$ and this is partly substantiated by carbon and platinum analyses. The compound gives a very dark green solution in dichloromethane.

Reactions of fluoroolefines with tri-n-butyl tin fluoride.

Since fluoro-olefines appear to add to certain metal-fluorine bonds perfluoroalkyl tin compounds might be obtained from tetrafluoroethylene and tri-n-butyl tin fluoride. However, no reaction occurs between these two compounds in methanol or anhydrous hydrogen fluoride.

Conclusions.

Although attempts to prepare olefine-platinum-fluoride complexes have failed so far, there is no reason why π -bonded ligand-metal-fluoride complexes should not exist provided that the correct method can be found for their preparation. One method which might prove successful is the replacement of chlorine with fluorine in olefine-metal

chloride complexes by reaction with hydrogen fluoride or silver fluoride and work along these lines will continue.

EXPERIMENTAL

Preparation of bromine trifluoride.

Bromine trifluoride was prepared by passing chlorine trifluoride through bromine contained in an iron bottle at 10°C. The chlorine trifluoride was contained in a cylinder kindly supplied by Imperial Chemical Industries Ltd.

Preparation of sodium fluoroplatinate.

Sodium fluoroplatinate was prepared by the addition of bromine trifluoride to sodium hexabromoplatinate suspended in bromine.¹³¹ Excess bromine and bromine trifluoride were removed under vacuum and the last traces of bromine trifluoride were removed under vacuum at 200°. The crude solid was dissolved in boiling water and heated for 5 minutes and filtered. Addition of alcohol to the filtrate precipitated the sodium fluoroplatinate which was filtered and dried under vacuum.

Preparation of sodium hexafluoromanganate(IV).

Sodium hexafluoromanganate was prepared by addition of bromine trifluoride to a suspension of a 2:1 mixture of sodium fluoride and manganous iodate in bromine.¹³² Bromine and bromine trifluoride were removed under vacuum at 200°.

Preparation of platinic fluoride.

Platinic fluoride was prepared by the addition of bromine trifluoride to platinic bromide suspended in bromine.¹³³ Bromine and bromine trifluoride were removed under vacuum at 200°.

Preparation of palladium trifluoride.

Palladium trifluoride was prepared from palladium bromide and bromine trifluoride¹³³ as described for platinic fluoride.

Preparation of olefines.

Ethylene, propylene, butadiene, hexafluoropropene and acetylene were used from cylinders of the gases. Cyclohexene, 1-pentene, 2-pentene, 1-octene, 1-octyne, cycloocta-1:5-diene and norbornadiene were dried overnight with molecular sieves and were redistilled before use.

Preparation of tetrafluoroethylene.

Tetrafluoroethylene was prepared by cracking teflon¹³² under vacuum at about 500° in a silica bottle.

Preparation of hexafluorobut-2-yne.¹⁴⁰

A 1-litre 3-necked flask fitted with a mercury sealed stirrer, a condenser cooled with an acetone cardice mixture and a dropping funnel was charged with 60 g. of zinc dust

and 80 ml. of acetic anhydride. The outlet of the condenser was connected to a trap cooled in liquid oxygen and the trap was protected from the air by a mixture of sodium hydroxide and calcium chloride. The mixture was heated to about 100° with vigorous stirring and a solution of 42 g. of 1,1,1,4,4,4-hexafluoro-2,2,3,3-tetrachlorobutane (kindly supplied by Halocarbon Products Inc.) in 50 ml. of acetic anhydride was added dropwise over a period of 4 hours. 30 g. of zinc dust was then added and the reaction was continued overnight. The hexafluorobut-2-yne was collected in the trap cooled in liquid oxygen and the acetylene was purified by distillation under vacuum.

Preparation of tetrakis(triphenylphosphine)platinum dihydride.

Tetrakis(triphenylphosphine)platinum dihydride¹³⁵ was prepared from potassium tetrachloroplatinite,¹³⁶ triphenylphosphine and potassium hydroxide.¹³⁶

Preparation of bis(triphenylphosphine)platinum difluoride.

Anhydrous hydrogen fluoride was condensed on to $(\text{Ph}_3\text{P})_4\text{PtH}_2$ contained in a polythene bottle.¹³⁹ The mixture was allowed to warm to room temperature and the excess hydrogen fluoride was removed in a stream of air.

The product was dissolved in dichloromethane and was precipitated by adding the solution to a large volume of ether. The compound was purified by this method three or four times.

Reactions of olefines and acetylenes with aqueous solutions of sodium fluoroplatinate.

Ethylene. A solution of sodium fluoroplatinate in water was shaken in an atmosphere of ethylene in a similar apparatus for that described for the preparation of Zeise's salt.¹³⁷

A yellow precipitate was formed almost immediately and after leaving overnight the precipitate was filtered and dried under vacuum.

Analysis: Found: Pt, 67.5; H, 2.6. Calc. for $\text{PtO}_2 \cdot 3\text{H}_2\text{O}$; Pt, 69.5%; H, 2.2%.

To verify that the hydrated platinum oxide precipitated was a derivative of platinum(IV), the yellow precipitate was dissolved in dilute hydrochloric acid and potassium chloride was added. The yellow precipitate was filtered and dried. The X-ray powder pattern of the compound was identical to that obtained from a pure sample of K_2PtCl_6 prepared from hexachloroplatinic acid and potassium chloride.

The solution obtained from the filtration of the platinic oxide had a definite smell of acetaldehyde but no derivative could be obtained with either 2:4 dinitrophenylhydrazine or semicarbazide. Presumably most of the acetaldehyde was lost due to its low solubility and high volatility. Addition of bis(ethylenediammine)platinum(II) dichloride to the solution gave a violet precipitate of $[\text{Pt}(\text{en})_2]\text{PtX}_4$ indicating the presence of a platinum(II) species present in solution. However, evaporation of the solution under vacuum gave a yellow solid which contained no carbon. Found: C, 0.1%; H, 2.3%.

Passage of ethylene through a solution of Na_2PtF_6 also induced hydrolysis of the fluoroplatinate but the reaction was slower than the pressure method.

Acetylene. Passage of acetylene through an aqueous solution of Na_2PtF_6 gave a precipitate of $\text{PtO}_2 \cdot 3\text{H}_2\text{O}$. Found: Pt, 69.8; H, 2.9%. No aldehyde or ketone could be detected in the resulting solution.

Cyclohexene. Cyclohexene gave a yellow precipitate of hydrated platinic oxide with an aqueous solution of sodium fluoroplatinate almost immediately. The mixture was shaken overnight and the water and organic material were removed by

distillation since the platinum in solution forms a complex with 2:4 dinitrophenylhydrazine. Addition of Brady's reagent to the distillate gave a precipitate which was recrystallised three times from alcohol, m.p. 158° , 160° , 160° (2:4 dinitrophenylhydrazone of cyclohexanone, m.p. 160°). In a typical experiment 10.4 g. of cyclohexene and 0.42 g. of Na_2PtF_6 in 10 mls. of water gave a 10% yield of cyclohexanone based on the amount of Na_2PtF_6 taken. In one experiment the distillate was extracted with ether.

The ether was removed by distillation and a nuclear magnetic resonance spectrum of the residue possessed a weak fluorine line. Presumably this could be due to cyclohexyl fluoride.

Butadiene. Butadiene was shaken with an aqueous solution of fluoroplatinate in a bomb overnight. A yellow precipitate presumed to be $\text{PtO}_2 \cdot x\text{H}_2\text{O}$ was formed and distillation of the solution gave a distillate which gave a positive test with Schiff's reagent indicating the presence of an aldehyde. Addition of Brady's reagent to the distillate gave a precipitate which was recrystallised twice from a benzene-petroleum ether mixture, m.p. 188° , 190° (2:4 dinitrophenylhydrazone of crotonaldehyde, m.p. 190°).

Other olefines and acetylenes. Tetrafluoroethylene, propylene, hexafluoropropene, 1-pentene, 2-pentene, 1-octene,

acetylene and hexafluorobut-2-yne all give yellow precipitates with aqueous solutions of sodium hexafluoroplatinate presumed to be hydrated platonic oxide. The solutions when distilled gave distillates which on addition of Brady's reagent gave a positive test indicating that a compound with a ketonic group was present. However, in each case the amount of derivative obtained was so minute that identification by conventional means was not possible. In the reaction with tetrafluoroethylene a large amount of teflon was produced.

Reaction of alkali with sodium hexafluoroplatinate.

Sodium hydroxide reacts with an aqueous solution of sodium fluoroplatinate to give a yellow precipitate presumed to be hydrated platonic oxide. The solution also goes a much darker yellow presumably due to the formation of complexes of the type $\text{Na}_n[\text{PtF}_{6-n}(\text{OH})_n]$ (where $n = 0, 1, 2, 3, 4, 5, \text{ or } 6$).

Reaction of cyclohexene with sodium hexafluoromanganate(IV).

Cyclohexene was shaken overnight with a solution of sodium fluoromanganate in 40% aqueous hydrogen fluoride. A dark brown precipitate which was presumed to be manganese dioxide was formed and the solution was neutralised with

sodium carbonate and distilled. The distillate gave a positive reaction with Brady's reagent but no derivative could be isolated.

Reactions of olefines with sodium fluoroplatinate in anhydrous solvents.

Cyclohexene was shaken overnight with suspensions of sodium fluoroplatinate in ether, tetrahydrofuran and diglyme (diethyleneglycol-dimethyl ether). (These ethers had all been dried with sodium and redistilled). The solutions obtained from the latter two solvents became slightly yellow in colour although most of the fluoroplatinate was insoluble. In each case evaporation of the solutions gave a small amount of a light yellow compound which analysed as unchanged Na_2PtF_6 . Found for reaction involving tetrahydrofuran, Pt, 45.0. Na_2PtF_6 requires Pt, 54.9%. Found for reaction involving diglyme Pt, 54.3%.

Cycloocta-1:5-diene was shaken overnight with sodium fluoroplatinate suspended in diglyme. Evaporation of the light yellow solution gave unchanged Na_2PtF_6 . Found: Pt, 53.9; Na_2PtF_6 requires Pt, 54.9%.

Sodium fluoroplatinate was found to be insoluble in vinyl and ethyl acetates but was slightly soluble in propionic acid.

Reactions of olefines and acetylenes with platinic fluoride.

Cyclohexene was heated gently with platinic fluoride suspended in benzene. The fluoride became black and the solid was filtered in the dry box. A similar reaction occurred when diphenylacetylene was used in the place of the olefine. Analysis of the black solids indicated that they were metallic platinum. Found for the cyclohexene experiment, Pt, 98%. Found for diphenylacetylene experiment, Pt, 96%.

Platinic fluoride in a bomb was left in contact with a pressure of ethylene overnight. A black solid was obtained which was unaffected by organic solvents and was presumed to be platinum.

Tetrafluoroethylene was heated with platinic fluoride in a bomb at 80° overnight. A black solid was obtained insoluble in organic solvents and boiling aqua regia. A similar product was obtained when the reaction was repeated in the presence of anhydrous hydrogen fluoride. The product was probably a mixture of metallic platinum and teflon.

Reaction of hexafluorobut-2-yne with platinic fluoride.

Platinic fluoride and hexafluorobut-2-yne were left in a bomb at room temperature overnight. A dark red solid was

obtained which was recrystallised from acetone to give a dark red compound. Found: C, 22.3; H, 2.4; Pt, 36.3%. (C:Pt = 1:10).

The infrared spectrum of the solid in a nujol mull was as follows (figures in microns). 7.61 - 9.5 (broad band with maxima at 8.10 and 8.78), 10.35w, 11.64w, 14.3w.

Reaction of hexafluorobut-2-yne with palladium trifluoride.

Hexafluorobut-2-yne and palladium trifluoride were left in a bomb at room temperature overnight. On opening the bomb two products were obtained. One was a red oil which was easily separated from the black solid present by extraction with dry "AnalaR" carbon tetrachloride. The carbon tetrachloride solution was evaporated to dryness to give the red oil. Found: C, 31.8; H, 2.1% $(C_4F_6)_n$ requires C, 29.6%. Mol.wt = 5081. Thus n is about 31.

The majority of the black solid is soluble in acetone to give a brown solution which deposits a black solid overnight. The infrared spectrum of the black solid has strong C-F bands at 8.05 and 8.82 μ . and further work on this compound is in progress.

Reaction of norbornadiene with bis(triphenylphosphine) platinum difluoride.

Norbornadiene (2 ml.) was refluxed for 30 minutes with a solution of $(\text{Ph}_3\text{P})_2\text{PtF}_2$ (0.3 g.) in dichloromethane (5 ml.). The solution became red and addition of ether precipitated a pink solid whose infrared spectrum was identical to that of $(\text{Ph}_3\text{P})_2\text{PtF}_2$. This colour change occurs when solutions of the phosphine are heated alone and this has been attributed to a cis-trans isomerisation.¹³⁹

Reaction of hexafluorobut-2-yne with $(\text{Ph}_3\text{P})_2\text{PtF}_2$.

Hexafluorobut-2-yne was heated with $(\text{Ph}_3\text{P})_2\text{PtF}_2$ in dichloromethane at 80° overnight. The solid appeared unchanged and the infrared spectrum of the solid in nujol was identical to the starting material.

Reaction of tetrafluoroethylene with $(\text{Ph}_3\text{P})_2\text{PtF}_2$.

Tetrafluoroethylene was heated with $(\text{Ph}_3\text{P})_2\text{PtF}_2$ in anhydrous hydrogen fluoride in a bomb at 150° overnight. The bomb was cooled and the hydrogen fluoride and tetrafluoroethylene were vented into a fume cupboard and the last traces of hydrogen fluoride were removed under vacuum. The black solid obtained was almost completely soluble in dichloromethane to give a very dark green solution. The dichloromethane was removed under vacuum and very dark green

crystals were obtained.. Analysis: Found: C, 48.2%; H, 2.8%; Pt, 20.6. $(\text{Ph}_3\text{P})_2\text{Pt}(\text{C}_2\text{F}_5)_2$ requires C, 50.2%; H, 3.2%; Pt, 20.3%. $(\text{Ph}_3\text{P})_2\text{PtF}(\text{C}_2\text{F}_5)$ requires C, 53.2%; H, 3.5%; Pt, 22.8%. The infrared spectrum of the compound was as follows (figures in microns).

4.67m, 7.68w, 8.36m, 8.46w, sh., 9.04w, 9.30w, sh., 9.83w, 10.25w, sh., 11.86w, 12.47w, 13.45m, 14.35w.

The band at 4.67 microns cannot be a carbonyl absorption. A similar band has been observed in the compound obtained from the reaction of $(\text{Ph}_3\text{P})_2\text{PtF}_2$ plus carbon disulphide.¹³⁰ This absorption might be a metal-hydride frequency but it seems strange that the hydride did not react with the hydrogen fluoride. This absorption may be an overtone due to a carbon-fluorine vibration although overtones are generally weaker than this band. Attempts to purify the compound by chromatography were unsuccessful. The compound dissolved in dichloromethane, but decomposed immediately on an alumina column (the alumina had previously been deactivated for 6 hours).

Reaction of tetrafluoroethylene with tri-n-butyl tin fluoride.

Tetrafluoroethylene was heated with tri-n-butyl tin fluoride in methanol in a bomb at 100° overnight.

On cooling and opening the bomb the white solid obtained was filtered and dried. Its infrared spectrum was identical to the original tri-*n*-butyl tin fluoride.

Similarly tetrafluoroethylene failed to react with tri-*n*-butyl tin fluoride suspended in anhydrous hydrogen fluoride in a bomb at 110° overnight.

APPARATUS USED IN COURSE OF WORK

Infrared spectra were measured on (i) a Perkin-Elmer double beam recording spectrophotometer, Model 21, using sodium chloride or potassium bromide optics, (ii) a Grubb Parsons double beam recording spectrophotometer, Type S₄ using sodium chloride optics and (iii) a Grubb Parsons double beam recording spectrophotometer using caesium iodide optics. Mull spectra were recorded between sodium chloride and potassium bromide plates.

Nuclear magnetic resonance spectra were recorded using an A40 Varian high resolution instrument working at 56.4 Mc/s (for F¹⁹) and 10 Mc/s (for B¹¹).

X-ray powder photographs were taken on a Metropolitan Vickers set incorporating a demountable target using a nine centimetre camera. Copper or cobalt targets were used throughout the work and the radiations were filtered through nickel and iron foil respectively. Samples were contained in Lindemann glass capillaries sealed with warm picein wax.

Analytical determinations for carbon, hydrogen and platinum were carried out by the Imperial College

Microanalytical Department. Analyses for organometallic derivatives of palladium and platinum were carried out by the staff of the Microanalytical Department of the Royal College of Science and Technology, Glasgow.

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