29. *The Halides of Niobium and Tantalum. Part VI.*[1]

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Complex formation between dimethyl sulphide, diethyl sulphide, and tetrahydrothiophen and niobium pentachloride and pentabromide, and tantalum pentachloride, pentabromide, and pentaiodide has been studied. The following crystalline 1 : 1 complexes have been isolated, and their compositions established by analysis and vapour-pressure measurements: $NbCl_5,Me_2S$; $NbBr_5,Me_2S$; $TaCl_5,Me_2S$; $TaBr_5,Me_2S$ (m. p. 108°); $NbCl_5,Et_2S$ (m. p. ~17°); $TaCl_5,Et_2S$ (liquid)—all of which distilled or sublimed unchanged—and $NbBr_5,Et_2S$, $TaBr_5,Et_2S$, and TaI_5,Et_2S which decomposed on heating into their original components. There was also some evidence for $TaCl_5,2Me_2S$, melting incongruently at about 15°.

The halides are more soluble in the sulphides than in diethyl ether, and the complexes more stable. There is very little splitting of the sulphide on heating.

Tetrahydrothiophen formed 1 : 2 complexes, *viz*: $NbCl_5,2[CH_2]_4S$, $NbBr_5,2[CH_2]_4S$, $TaCl_5,2[CH_2]_4S$, $TaBr_5,2[CH_2]_4S$, and $TaI_5,2[CH_2]_4S$. Except for $TaI_5,2[CH_2]_4S$ these were insoluble in tetrahydrothiophen.

VERY few compounds of niobium or tantalum are known in which the metal is bonded directly to sulphur. The only sulphur-containing complexes of either metal which appear

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[1] Part V, Cowley, Fairbrother, and Scott, *J.*, 1958, 3133.

to have been reported[2] are $NbCl_5,SCl_4$ and $TaCl_5,SCl_4$, formed as by-products in the reaction between the pentoxides and thionyl chloride, or prepared by heating the pentachlorides with sulphur dichloride and chlorine in a sealed tube. Both compounds were very sensitive to moisture and decomposed easily on heating into their components.

More recently, Niel'son[3] has studied the reaction of thiophosphoryl chloride with niobium and tantalum pentachlorides. It was found that, in contrast to phosphoryl chloride which forms stable complexes with these halides, no complex formation could be detected with thiophosphoryl chloride.

In Part V[1] of this series we examined the interaction of diethyl ether with these pentachlorides and bromides and observed the formation of 1 : 1 complexes which showed small but measurable dissociation pressures at room temperatures, and which readily (at about 100°) decomposed into ethyl halide and metal oxytrihalide. We have now examined the reactions of the pentachlorides and pentabromides, and of tantalum pentaiodide, with dimethyl sulphide, diethyl sulphide, and tetrahydrothiophen. Complex formation has been established both by phase studies (composition–vapour pressure relations) and by analysis of the crystalline complexes. Measurements have also been made of the solubilities of these halides in dimethyl sulphide, and of tantalum pentaiodide in diethyl sulphide.

The most noticeable features of these reactions were the greater solubilities of the halides in dimethyl and diethyl sulphide, and the greater thermal stability of the adducts compared with the oxygen-ether complexes when heated *in vacuo*; the sulphide complexes distilled or sublimed unchanged or decomposed into their original components. Splitting of the sulphide or formation of $NbSX_3$ or $TaSX_3$ was either very small or entirely absent. With dimethyl and diethyl sulphides, only 1 : 1 complexes were observed, except in the case of tantalum pentachloride which gave evidence of a 1 : 2 complex melting incongruently at about 15°. This does not necessarily exclude the formation of other 1 : 2 complexes at lower temperatures. With tetrahydrothiophen only 1 : 2 complexes were observed, which were insoluble in excess of the ligand. On heating these *in vacuo* extensive charring occurred and only a very small amount of sublimate was formed.

EXPERIMENTAL

Preparation of Halides.—The pentachlorides and pentabromides were prepared as described in Part V.[1] Tantalum pentaiodide was prepared in part by the method of Alexander and Fairbrother[4] and in part by the more convenient method described by Rolsten.[5] All the halides were purified by fractional sublimation and sealed *in vacuo* into fragile hook-ended ampoules from which they were sublimed into the reaction system.

Sulphides.—These were purified by fractional distillation and collected over narrow ranges: dimethyl sulphide, b. p. 37·4°/766·3 mm.; diethyl sulphide, b. p. 90·5°/744·9 mm.; tetrahydrothiophen, b. p. 121·0°/753·4 mm. Rigorous drying was effected by means of lithium aluminium hydride, and by pretreatment with the halide under examination.

Vapour-pressure Measurements.—These were carried out in a conventional apparatus, with minor modifications as described in Part V. However, the dissociation pressures of the 1 : 1 complexes, when all excess of solvent had been removed, were so small that it was quite impracticable to estimate their variation with temperature. It was therefore clear that they were more stable than the diethyl ether complexes described in Part V.

X-*Ray Examination.*—Powder diffraction photographs were taken, by using nickel-filtered Cu-K_α radiation and a 11·4 cm. Philips camera, of specimens enclosed in 0·5 mm. diam. Lindemann glass tubes.

Solubility Measurements.—These were carried out in an all-glass sealed apparatus, essentially by the technique described by Fairbrother, Scott, and Prophet.[6] A great improvement was

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[2] Funk and Weiss, *Z. anorg. Chem.*, 1958, **295**, 327.

[3] Niel'son, *Russ. J. Inorg. Chem.*, 1960, **5**, 794.

[4] Alexander and Fairbrother, *J.*, 1949, 2472.

[5] Rolsten, *J. Amer. Chem. Soc.*, 1958, **80**, 2952.

[6] Fairbrother, Scott, and Prophet, *J.*, 1956, 1164.

effected by the use of lithium aluminium hydride as a drying agent. This reagent, which infrared absorption measurements showed to be without effect on the sulphides, reduced the necessary pre-treatment with the halide under observation to a single stage immediately before the solubility cell. As in the studies with ethyl ether a small amount of the sulphide was condensed from the remaining solution at the conclusion of each run and the absence of decomposition confirmed by infrared spectroscopy.

Thermal Stabilities.—Specimens of complex were heated, in a tube attached to a vacuum line, at various temperatures controlled by a Cambridge thermocouple regulator. Provision was made for the condensation of any gaseous products into a removable tube provided with a tap, and which could be transferred to a mass spectrometer for analysis.

System Niobium Pentachloride–Dimethyl Sulphide.—Niobium pentachloride dissolved readily to give a dark red solution which on concentration deposited pale yellow crystals (Found: C, 7·8; H, 1·3; Cl, 51·8; Nb, 28·2. $NbCl_5,Me_2S$ requires C, 7·2 H, 1·8; Cl, 53·4; Nb, 28·0%). Vapour-pressure measurements at 24·0° indicated a 1 : 1 complex. When the solid was heated *in vacuo* to 280° it darkened slightly and a pale yellow sublimate formed. The solid did not melt and no detectable gaseous decomposition products were observed. The *X*-ray powder photograph of the sublimate was identical with that of the original complex.

System Niobium Pentabromide–Dimethyl Sulphide.—Niobium pentabromide dissolved readily to give a dark red-brown solution which on concentration deposited orange-brown crystals [Found: C, 6·9; H, 1·5; Br, 64·3; Nb, 15·9. $NbBr_5,Me_2S$ requires C, 4·3; H, 1·3; Br, 72·0; Nb, 16·7%. Vapour-pressure measurements at 20·6° indicated a 1 : 1 complex. When this was heated *in vacuo* an orange sublimate was formed from about 120° upwards. No melting occurred up to 200° and very little charring. At this temperature a small amount of condensable gas was evolved, identified by the mass spectrometer as chiefly dimethyl sulphide. There was a hint of the presence of a trace of methyl bromide which suggested that at a much higher temperature some splitting of the sulphide might occur.

System Tantalum Pentachloride–Dimethyl Sulphide.—Tantalum pentachloride dissolved very readily to give a red solution which at room temperature deposited crystals of an almost white complex, $TaCl_5,Me_2S$. Vapour-pressure measurements also at 23·0° indicated a 1 : 1 complex, with no evidence for a 1 : 2 complex (Found: C, 5·8; H, 1·4; Cl 41·6; Ta, 45·0. $TaCl_5,Me_2S$ requires C, 5·7; H, 1·4; Cl, 42·2; Ta, 43·0%).

This system however exhibited an exceptional behaviour. Tantalum pentachloride is extremely soluble in dimethyl sulphide, dissolving in less than one third of its own weight of solvent at room temperature. On slight cooling of a solution, saturated at above 15°, the whole system solidified. On re-heating it to above 15°, the solid which separated from solution on removal of excess of solvent was found to be the 1 : 1 complex. Since the composition of the liquid phase at 15·0° was very nearly that of a 1 : 2 *complex* [g. of $TaCl_5$: g. of $Me_2S = 2{\cdot}96$. $TaCl_5,2Me_2S$ requires 2·89] these observations point to the formation of a 1 : 2 *complex* which melts incongruently at about 15°. Pale yellow crystals, deposited at 0° by concentration under vacuum of a dilute solution, and drained from mother liquor through a sintered disc, gave Cl, 37·95, 37·9. $TaCl_5,2Me_2S$ requires Cl, 36·75%. This analysis is much closer to that of a 1 : 2 than to a 1 : 1 complex, the slightly high chlorine content probably being due to loss of solvent during transfer.

These observations, together with the formation of 1 : 2 complexes with tetrahydrothiophen (described below), suggest that other 1 : 1 complexes with dimethyl sulphide might be formed at lower temperatures. This merits further investigation.

The pale yellow 1 : 1 complex did not melt when heated to 150° under nitrogen at atmospheric pressure, but began to sublime at this temperature, with slight charring. The complex could be sublimed easily *in vacuo* at 120°, the *X*-ray powder photograph being identical with that of the unsublimed complex. No gaseous decomposition products could be detected.

Many of the crystals of the 1 : 1 complex which separated from solution at room temperature were several mm. in size, clear, and well formed. They could be handled in air but slowly hydrolysed, becoming opaque. Suitable crystals were mounted in Lindemann glass tubes for *X*-ray examination and were then satisfactory for use during several weeks. Crystals were mounted on a Nonuis single-crystal camera, diameter 57·3 mm., and oscillation and equi-inclination Weissenberg photographs taken, unfiltered Co radiation being used. Photographs were taken with the crystal mounted on each of the three axes.

It was hoped to accomplish a full structure determination but this has proved impracticable in the time available. It was however established that the crystals of the $TaCl_5,Me_2S$ complex are orthorhombic, belonging to space group either *Pnma* or *Pna*2_1, and that there are four molecules of $TaCl_5,Me_2S$ in the unit cell whose dimensions are: $a = 15{\cdot}7$, $b = 7{\cdot}4$, $c = 11{\cdot}6$ Å; $d = 2{\cdot}3$, $2{\cdot}12$ (calc. 2·19).

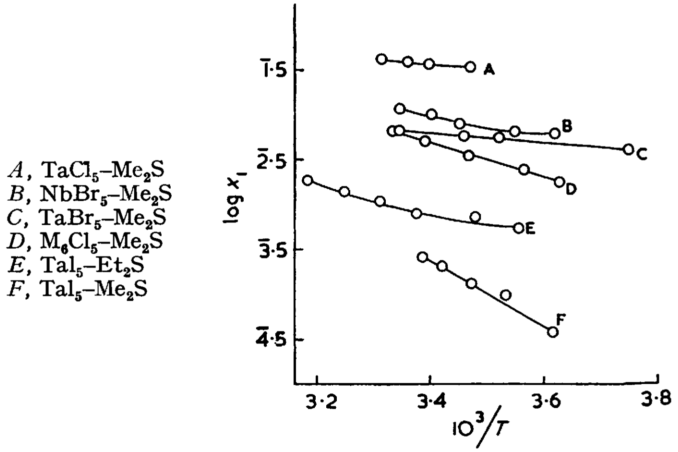
System Tantalum Pentabromide–Dimethyl Sulphide.—Tantalum pentabromide dissolved very easily to give a cherry-red solution which on concentration deposited yellow crystals. (Found: C, 3·6; H, 1·0; Br, 61·4; Ta, 25·9. $TaBr_5,Me_2S$ requires C, 3·7; H, 0·9; Br, 62·2; Ta, 28·1%). Vapour-pressure measurements at 22·5° indicated a 1 : 1 *complex*. The yellow complex melted at ~108°, without decomposition, to give a liquid with a low vapour pressure since sublimation *in vacuo* on to the cool parts of the tube only became appreciable at about 200°. Only very little gaseous product was evolved and this was shown by the mass spectrometer to be dimethyl sulphide. The *X*-ray powder photograph of the sublimate was identical with that of the original complex. Similar results were obtained when the complex was heated to 300° *in vacuo*.

Solubilities.—In the Table are given the solubilities (*s*) as g. of halide dissolved by 100 g. of dimethyl sulphide and in the Figure the log mole-fraction of solute (x_1) as a function of $1/T$.

$NbCl_5$		$NbBr_5$		$TaCl_5$		$TaBr_5$		TaI_5	
t	*s*	*t*	*s*	*t*	*s*	*t*	*s*	*t*	*s*
2·6°	7·89	3·1°	52·91	15·0°	295·8	−6·4°	40·83	3·3°	0·49
7·3	10·85	8·7	55·39	21·4	333·0	3·2	54·34	9·9	1·28
15·2	16·14	16·6	67·00	24·6	366·2	10·8	55·98	14·8	1·68
22·1	23·95	21·0	88·66	28·7	398·5	16·0	57·42	19·0	2·72
26·9	30·53	25·8	102·4			26·0	66·41	22·2	3·35

These results show some extraordinary and unexplained variations.

Whereas the solubility of niobium pentachloride in dimethyl sulphide is of the same order as that in diethyl ether, the solubility of tantalum pentachloride is more than ten times as great, and whereas niobium pentabromide is several times less soluble than niobium pentachloride in ether, in dimethyl sulphide the reverse is true. It may be recalled however that, within the present temperature range, tantalum pentachloride is the only halide which gives evidence of the formation of a 2 : 1 complex.



System Niobium Pentachloride–Diethyl Sulphide.—Niobium pentachloride dissolved very readily to give a red solution which on concentration deposited yellow crystals of the 1 : 1 complex (Found: C, 13·1; H, 2·7; Cl, 48·2; Nb, 26·0. $NbCl_5,Et_2S$ requires C, 13·4; H, 2·8; Cl, 48·6; Nb, 25·8%).

This complex melted at 17° and consequently tended to liquefy when handled. In consequence, attempts to obtain a satisfactory *X*-ray powder photograph proved unsuccessful. On heating *in vacuo* at about 10^{-5}—10^{-6} mm. the crystals melted to a red liquid which at 170° refluxed in the tube without decomposition.

System Niobium Pentabromide–Diethyl Sulphide.—Niobium pentabromide dissolved readily to give a red solution which deposited a brown complex on concentration (Found: C, 9·1; H, 1·85; Br, 67·8; Nb, 16·6. $\mathrm{NbBr_5,Et_2S}$ requires C, 8·25; H, 1·7; Br, 68·6; Nb, 16·0%). Vapour-pressure measurements at 37·6° also indicated the formation of a 1 : 1 *complex*. When heated in a vacuum the complex did not melt but darkened in colour above 150° and gave a dark brown sublimate. Hardly any charring occurred. An *X*-ray powder photograph of the sublimate showed that it was niobium pentabromide. Mass-spectrometer analysis of the gaseous product showed it to consist of 98% of diethyl sulphide and 2% of ethyl bromide. The complex therefore dissociates into its components before any appreciable splitting of the ligand occurs.

System Tantalum Pentachloride–Diethyl Sulphide.—Tantalum pentachloride dissolved readily to give a cherry-red solution which on concentration gave the 1 : 1 *complex*, a liquid at room temperature (Found: Cl, 40·0; Ta, 39·7. $\mathrm{TaCl_5,Et_2S}$ requires Cl, 39·6; Ta, 40·4%). Vapour-pressure measurements at 37·6° also indicated a 1 : 1 complex, which was isolated as a liquid by pipetting it from the reaction flask when the pressure had fallen below 1 mm. and no more diethyl sulphide could be pumped off. The melting point was not determined but lies well below 0°. When heated *in vacuo*, the complex distilled without evidence of decomposition.

System Tantalum Pentabromide–Diethyl Sulphide.—Tantalum pentabromide dissolved readily to give a cherry-red solution which deposited, on concentration, yellow crystals of the *complex* $\mathrm{TaBr_5,Et_2S}$ (Found: C, 7·2; H, 1·5; Br, 59·8; Ta, 26·9. $\mathrm{TaBr_5,Et_2S}$ requires C, 7·1; H, 1·5; Br, 59·6; Ta, 27·0%). Vapour-pressure measurements at 37·6° also indicated a 1 : 1 complex. This complex did not melt when heated, but at 200° *in vacuo* gave a yellow crystalline sublimate of $\mathrm{TaBr_5}$ (*X*-ray powder photograph). Mass-spectrometer examination of the gaseous decomposition products indicated the presence of diethyl sulphide (95%) and ethyl bromide (5%).

System Tantalum Pentaiodide–Diethyl Sulphide.—Tantalum pentaiodide, the least soluble of these halides, was rather more soluble in diethyl sulphide, in which it gave a dark red solution, than in diethyl ether and much more so than in dimethyl sulphide. The dark brown solid which separated from the vapour pressure run at 37·6°, which also indicated the formation of a 1 : 1 *complex*, had the approximate composition $\mathrm{TaI_5,Et_2S}$, being still contaminated with a little excess of solvent (Found: C, 8·2; H, 1·8; I, 63·4; Ta, 18·4. $\mathrm{TaI_5,Et_2S}$ requires C, 5·3; H, 1·1; I, 70·0; Ta, 20·0%.) When heated *in vacuo* the solid did not melt and no sublimate was formed below 200°. As the temperature was raised further an increasing amount of a dark black sublimate of tantalum pentaiodied was formed. The only gaseous product identified was diethyl sulphide.

Solubility (*s*) of tantalum pentaiodide in diethyl sulphide (measured as g. per 100 g.).

t	8·0°	14·2°	22·9°	28·8°	34·6°	40·8°
s	5·09	6·62	7·14	9·84	12·55	17·23

Direct measurements of the solubilities in diethyl sulphide of the other four halides were not made, chiefly on account of the higher viscosities and lower vapour pressures of the saturated solutions which made the sintered-disc technique difficult to operate.

Systems with Tetrahydrothiophen.—The pentachlorides and pentabromides, when brought into contact with this solvent, all dissolved initially to some extent and gave solutions which were red or orange. After a few moments, however, reaction occurred and yellow to brown crystalline solids were precipitated, which gave satisfactory *X*-ray powder photographs with varying degrees of microcrystallinity indicated. The supernatant liquid became almost colourless and free from dissolved halide. The separated solids were removed for analysis and shown to consist of 1 : 2 complexes. However, they were all extremely hygroscopic and fumed in the air, especially the bromide and iodide complexes. This hydrolysis is undoubtedly the source of consistently high metal and low halide values in the analyses. The compositions however were sufficiently close to indicate the formation of 1 : 2 complexes. In general the amount of charring on heating *in vacuo* was very much greater, and the amount of sublimate obtained very much less, than in the case of the dimethyl sulphide complexes.

Niobium pentachloride. This formed a brownish yellow *complex* (Found: C, 21·7; H, 3·8; Cl, 37·4; Nb, 23·4. $\mathrm{NbCl_5,2C_4H_8S}$ requires C, 21·5; H, 3·6; Cl, 39·7; Nb, 20·8%). When the complex was heated *in vacuo*, charring began at 150° and was very extensive at 360°. Only a small quantity of sublimate was obtained which gave an indistinct *X*-ray powder photograph different from that of the original complex and from niobium pentachloride. A microanalysis of the sublimate (Found: C, 10·5; H, 2·7%) suggests that the sublimate may be a 1 : 1 complex.

Niobium pentabromide. The pentabromide formed a dark orange microcrystalline complex. which could be deduced from the broadening of the *X*-ray diffraction lines (Found: C, 14·2; H, 2·4; Br, 56·6; Nb, 14·6. $NbBr_5,2C_4H_85$ requires C, 14·4; H, 2·4 Br, 59·8; Nb, 13·8%). When it was heated *in vacuo* little was observed below 100° where extensive charring and a little sublimation occurred. An *X*-ray photograph of the sublimate was inconclusive (Found: C, 5·2; H, 2·7%).

Tantalum pentachloride. This gave a very pale yellow *complex* (Found: C, 15·8; H, 2·8; Cl, 32·4; Ta, 34·0. $TaCl_5,2C_4H_8S$ requires C, 18·0; H, 3·0; Cl, 33·2; Ta, 33·9%). When it was heated *in vacuo* extensive charring occurred at 200°. A very small amount of sublimate (Found: C, 4·7; H, 1·7%) was obtained.

Tantalum pentabromide. This gave a light orange *complex* (Found: C, 14·1; H, 2·4; Br, 49·7; Ta, 24·4. $TaBr_5,2C_4H_8S$ requires C, 12·7; H, 2·1; Br, 49·7; Ta, 23·9%). When heated *in vacuo* the complex was unaffected below 200° and no solid sublimed even at 350° although charring was extensive. The only gaseous product was tetrahydrothiophen.

Tantalum Pentaiodide. Tantalum pentaiodide, in contrast to the other halides, dissolved in tetrahydrothiophen to give a dark red solution which on concentration gave a dark brown/black solid which did not fume in air or appear to be hygroscopic. It was however difficult to remove all excess of solvent, and despite repeated grinding and powdering a satisfactory *X*-ray powder diffraction photograph was not obtained, though the pentaiodide itself and TaI_5,Et_2S did so [Found: C, 12·3; H, 2·2; I, 62·2; Ta, 19·1. $TaI_5,2C_4H_8S$ requires C, 9·7; H, 1·6; I, 63·0; Ta, 18·3%].

The *complex* decomposed above 150°; iodine vapour was evolved, but no other sublimate.

DISCUSSION

The most striking feature of these results is the high thermal stability of the sulphide complexes, which is much greater than that of the complexes with ethyl ether. A strict comparison of the stabilities of the tetrahydrothiophen complexes with those of tetrahydrofuran is not possible since both the pentachlorides and pentabromides break open the tetrahydrofuran ring and form polymers.[7]

Both the present pentachlorides and the pentabromides are Friedel–Crafts-type catalytic metal halides,[1] and therefore Lewis acids. Towards the more familiar Lewis acids of Group III, BX_3 and AlX_3, where X is a halogen or an alkyl group, the base strength of Group VI dialkyls decreases in the direction $OR_2 > SR_2$.[8,9] On the other hand there are a number of elements, such as the later transition metals, copper and zinc, and especially platinum and palladium, whose salts form stronger adducts with sulphides than they do with oxygen-ethers.[8] It is known [10] that if an acceptor atom possesses a complete *d*-shell of electrons in the penultimate group, these electrons may contribute to a supplementary binding. It is this class of atoms in general which form their most stable complexes with the second or subsequent atom of a ligand group.

In these pentahalides however all the readily available *d*-electrons of the metal atom are used in bonding with the halogen atoms. It is therefore remarkable that they too form stronger bonds with sulphur in sulphides than they do with oxygen and some other explanation than the use of filled *d*-orbitals must be sought.

In this connection it may be noted that Me_2S,BH_3 is more stable than Me_2O,BH_3 and $[CH_2]_4S{\cdot}BH_3$ than $[CH_2]_4O{\cdot}BH_3$,[11] although with boron trifluoride the oxygen-ether adducts are more stable than the sulphur ones. This reversal with borine, of the more familiar behaviour of a decrease in ability of Group VI atoms to form classical dative

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[7] Cowley, Ph.D. Thesis, Manchester 1956.

[8] Ahrland, Chatt, and Davies, *Quart. Rev.*, 1958, **12**, 265.

[9] Coyle, Kaesz, and Stone, *J. Amer. Chem. Soc.*, 1959, **81**, 2989.

[10] Pauling, " The Nature of the Chemical Bond," Ithaca, Cornell University Press, 1939, p. 231.

[11] Burg and Wagner, *J. Amer. Chem. Soc.*, 1954, **76**, 3307.

bonds with increasing atomic size, has been explained[12] as resulting from additional π bonding resulting from the overlap of the empty $3d$ orbitals of sulphur with a filled *pseudo* p_π orbital provided by the three hydrogen atoms of the borine group. Oxygen, on the other hand, has no d orbitals to offer. The conformity to the usual pattern, of boron trifluoride in contrast to borine, may be due to the electronegativity of the fluorine which prevents a drift of electron density towards the donor ligand. Similarly, it has been suggested[13] that the existence of OC,BH_3 and F_3P,BH_3 compared with the non-existence of their boron fluoride analogues may be due " to the inability of the deeply buried boron–fluorine bonding electrons to contribute to the empty $2p_\pi$ orbital in carbon monoxide, or to the $3d_\pi$ orbitals of phosphorus trifluoride, in a manner perhaps possible for boron–hydrogen electrons."

The pentachlorides and pentabromides of niobium and tantalum, in the gas phase, possess a trigonal bi-pyramidal structure with an electron configuration spd^3 or sp^3d.[14] No structural data for the pentafluorides are available nor any details of their co-ordination compounds, though they are excellent Friedel–Crafts-type catalysts.[15] It will be interesting to examine the relative stability of oxygen- and sulphur-ether adducts of these pentafluorides to determine whether the presence of the more electronegative fluorine atoms brings about a return to the $O > S$ sequence.

The second point which emerges is the formation of 1 : 2 complexes with the sterically unhindered tetrahydrothiophen. The question whether these are ionic with a co-ordination number of six, *viz.*, $[MX_4,2[CH_2]_4S]^+ X^-$ or covalent with a co-ordination number of seven, is as yet unresolved. Experiments to this end are difficult because the complexes do not melt without decomposition and, with the exception of the tantalum pentaiodide complex, are insoluble in tetrahydrothiophen. The possibility that these complexes add to the number, still fairly small, of niobium and tantalum compounds in which a co-ordination number of seven may be presumed, cannot however be excluded. The existence of this generally unusual co-ordination number is well known in the hepta-fluoride ions NbF_7^- and TaF_7^-.

Other cases include the adducts of two pyridine or two pyrimidine molecules to one of tantalum pentachloride reported by Linder and Feit,[16] those of two pyridine molecules to one of niobium or tantalum pentafluoride reported by Clark and Emeléus[17] and $TaCl_5,2NMe_3$ reported by Carnell and Fowles.[18] In the last case the sterically hindered triethylamine only gives a 1 : 1 adduct. A number of organic hydroxy-derivatives of niobium and tantalum, such as those with catechol, $(NH_4)_3[NbO(C_6H_4O_2)_3]$, and with acetylacetone, $(NH_4)_4[NbO(C_5H_6O_2)_3]$,[19] also are believed to be seven-co-ordinate.

We are indebted to the D.S.I.R. for a maintenance grant (to J. F. N.), and to Mr. O. S. Mills of this department for assistance with the crystallographic analysis of $TaCl_5,Me_2S$.

THE UNIVERSITY, MANCHESTER, 13. [*Received, June 5th,* 1961.]

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[12] Graham and Stone, *J. Inorg. Nuclear Chem.*, 1956, **3**, 164.
[13] Stone, *Chem. Rev.*, 1958, **58**, 119.
[14] Skinner and Sutton, *Trans. Faraday Soc.*, 1940, **36**, 668.
[15] Fairbrother and Frith, *J.*, 1951, 3051.
[16] Linder and Feit, *Z. anorg. Chem.*, 1924, **132**, 10.
[17] Clark and Emeléus, *J.*, 1958, 190.
[18] Carnell and Fowles, *J.*, 1959, 4113.
[19] Rosenheim and Roehrich, *Z. anorg. Chem.*, 1932, **204**, 342.