122. *The Halides of Niobium and Tantalum. Part IX.*[1] *Dimethyl Ether, Diethyl Ether, Dimethyl Sulphide, Diethyl Sulphide, and Tetrahydrothiophen Complexes of the Pentafluorides.*

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The following new 1 : 1 complexes have been prepared and their compositions established by analysis and vapour pressure studies: NbF_5,Me_2O; TaF_5,Me_2O; NbF_5,Me_2S; TaF_5,Me_2S; NbF_5,Et_2O; TaF_5,Et_2O; NbF_5,Et_2S; TaF_5,Et_2S. All of them can be distilled unchanged at low pressures. The first four are solid at room temperature and melt below 100°; the remaining four are liquids. The dimethyl sulphide adducts also sublime below their melting points. Vapour pressure studies indicate in addition the existence, at lower temperatures, of 1 : 2 adducts with dimethyl ether and dimethyl sulphide. Tetrahydrothiophen forms, with both pentafluorides, 1 : 2 adducts which melt below 100° with decomposition. Measurements have been made of the densities, viscosities, and electrical conductivities of molten diethyl ether and diethyl sulphide adducts; these indicate some degree of polymerisation and ionisation.

Prior to the present investigation, the only adducts of niobium and tantalum pentafluorides that had been reported are those with bromine trifluoride,[2] selenium tetrafluoride,[3] and with some nitrogen bases. Niobium pentafluoride reacts with pyridine, ammonia,[4] and ethylenediamine,[5] to form $NbF_5,2py$, $NbF_5,2NH_3$, and $NbF_5\ en_{1\cdot6}$; only the tantalum analogue of the first of these seems to have been reported.[4] It is noteworthy that in these reactions niobium pentafluoride, in contrast to the other pentahalides, undergoes neither ammonolysis with ammonia [6] nor reduction to Nb^{4+} with pyridine; [7] a similar reduction to Nb^{4+} and Ta^{4+} has recently been shown to occur with the bidentate ligands bipyridyl and 1,10-phenanthroline.[8] No adducts have been reported in which the donor atom is either oxygen or sulphur.

[1] Part VIII, preceding Paper.
[2] Gutmann and Emeléus, *J.*, 1950, 1046.
[3] Bartlett, *Progr. Inorg. Chem.*, 1960, **2**, 193.
[4] Clark and Emeléus, *J.*, 1958, 190.
[5] Cavell and Clark, *J. Inorg. Nuclear Chem.*, 1961, **17**, 257.
[6] Fowles and Pollard, *J.*, 1952, 4938.
[7] McCarley and Torp, *Inorg. Chem.*, 1963, **2**, 540.
[8] Allbutt, Feenan, and Fowles, *J. Less-Common Metals*, 1964, **6**, 299.

In Parts V—VII [9-11] the reactions of niobium and tantalum pentachlorides and pentabromides with some ethers and organic sulphides were described. It was shown that in these reactions diethyl and di-n-propyl sulphides form stronger adducts with these pentahalides than do the corresponding ethers. This work has now been extended to the pentafluorides, which form stable 1 : 1 adducts with dimethyl and diethyl ethers and sulphides. We have also examined the densities, viscosities, and conductivities of the molten diethyl ether and diethyl sulphide complexes.

EXPERIMENTAL

Pentafluorides.—These were prepared as previously described, by the action of gaseous fluorine on the pure metals, followed by fractional sublimation and transfer into small ampoules.

Ethers and Sulphides.—These were purified as described in Part VII.[11]

Vapour Pressure Measurements.—These were carried out in a conventional apparatus, with minor modifications.[9] For systems involving dimethyl ether, measurements were made at −63·5° (chloroform mush) and at −9·3° (ethylene glycol mush), for those involving diethyl ether or dimethyl sulphide at about 20°, and for diethyl sulphide and tetrahydrothiophen systems at 30°; the temperatures were maintained to ±0·05° during each vapour-pressure–composition run.

Preparation of Complexes.—After the demonstration of the composition of the complexes by vapour-pressure–composition measurements and analyses, the complexes were prepared, for density, viscosity, and conductivity measurements, on a 10 g. scale, by condensing a stoicheiometric amount of ligand on to a weighed quantity of halide at −195° in a vacuum. The system was then allowed to come slowly to room temperature, where the formation of the complex was usually complete within about 2 hr., the vessel being occasionally shaken and cooled to prevent further rise of temperature occasioned by the exothermicity of the reactions.

Conductivity Measurements.—Complexes were transferred in the liquid state, under a vacuum, to an attached Pyrex conductivity cell with bright platinum electrodes and which held about 2 ml. of liquid complex. The cells were calibrated by the use of 10^{-3}M-potassium chloride solution, typical cell constants being 10·08 and 7·278 cm.$^{-1}$. Measurements were made, with the cell totally immersed in water thermostat-controlled to ±0·01°, by means of a Wayne Kerr Universal Bridge B221, at 1592 c./sec. The precision of measurement at any one temperature was ±0·02% with an overall precision of ±0·1%.

Density and Viscosity.—Measurements were carried out as described in Part VIII.[1]

Niobium Pentafluoride–Dimethyl Ether System.—Niobium pentafluoride dissolved in an excess of dimethyl ether at −63·5° to give a clear solution which, on concentration, deposited colourless crystals and showed a break in the vapour-pressure–composition curve at $NbF_5,2Me_2O$. The dissociation pressure of this complex was negligible at −63·5° but was more than 1 atm. at room temperature. One mole of ether was lost at −9·3°, to give the colourless crystalline *complex* NbF_5,Me_2O, which melted at 31·5° and distilled unchanged at about 55°/10^{-3} mm. (Found: C, 10·3; H, 2·6; F, 43·1; Nb, 39·9. NbF_5,Me_2O requires C, 10·3; H, 2·6; F, 40·6; Nb, 39·7%).

Tantalum Pentafluoride–Dimethyl Ether System.—This system behaved almost exactly like the previous one; at −63·5° colourless crystals of $TaF_5,2Me_2O$ were deposited which lost ether at −9·3° to give the *complex* TaF_5,Me_2O, which melted at 80·0° and distilled unchanged at about 130°/$\sim10^{-3}$ mm. (Found: Ta, 56·4; F, 30·3. TaF_5,Me_2O requires Ta, 56·2; F, 29·5%). A mass spectrum of the small amount of gas liberated in the distillation showed it to consist only of dimethyl ether, with no trace of methyl fluoride.

Niobium Pentafluoride–Dimethyl Sulphide System.—Niobium pentafluoride dissolved in dimethyl sulphide at room temperature to give a light yellow solution which, on concentration, deposited colourless crystals. A break in the vapour-pressure–composition curve at 24·4° indicated the formation of unstable $NbF_5,2Me_2S$, with a dissociation pressure of about 35 cm. Further removal of sulphide gave colourless *crystals* of NbF_5,Me_2S (Found: C, 9·7; H, 2·5; F, 37·3; Nb, 37·1. NbF_5,Me_2S requires C, 9·6; H, 2·4; F, 37·9; Nb, 37·1%). When this was heated in a vacuum, a colourless crystalline sublimate formed at 35° and the solid melted at

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[9] Cowley, Fairbrother, and Scott, *J.*, 1958, 3133.
[10] Fairbrother and Nixon, *J.*, 1962, 150.
[11] Copley, Fairbrother, and Thompson, *J.*, 1964, 315.

76·2°. The sublimate had an *X*-ray powder photograph identical with that of the complex, and the small amount of gaseous product evolved in the sublimation was shown from its mass spectrum to be dimethyl sulphide. Some charring of the liquid complex occurred when heated at 95°.

Tantalum Pentafluoride–Dimethyl Sulphide System.—The behaviour of this system at 21·7° was very similar to that of the niobium pentafluoride–dimethyl sulphide system. The vapour-pressure–composition curve showed a break indicating the formation of unstable $TaF_5,2Me_2S$, with a dissociation pressure of about 25 cm. This lost sulphide to give the colourless crystalline complex TaF_5,Me_2S. When this was heated in a vacuum, a colourless crystalline sublimate formed at 44·5° and the complex melted at 66·5°; charring occurred above 75°. An *X*-ray powder photograph was identical with that of the original complex and showed them to be isomorphous with the NbF_5,Me_2S complex.

Niobium Pentafluoride–Diethyl Ether System.—Niobium pentafluoride dissolved readily in excess of diethyl ether at room temperature to give a red solution. Removal of the ether at 19·8° gave no sharp break in the vapour-pressure–composition curve since the complex was liquid at that temperature, but the curve cut the axis at a point corresponding to the *complex* NbF_5,Et_2O (Found: Nb, 35·65. NbF_5,Et_2O requires Nb, 35·5%). The light red liquid complex melted at $-7{\cdot}8°$ and distilled unchanged at about $55°/{\sim}10^{-3}$.

Tantalum Pentafluoride–Diethyl Ether System.—This system behaved in a similar manner to the last, giving a light red liquid *complex*, m. p. $-17{\cdot}8°$, which distilled unchanged at about $90°/{\sim}10^{-3}$ (Found: Ta, 51·9. TaF_5,Et_2O requires Ta, 51·65%). When heated to 135° at a higher pressure it decomposed completely.

Niobium Pentafluoride–Diethyl Sulphide System.—Niobium pentafluoride dissolved in diethyl sulphide to give a light yellow solution which, on concentration in a vacuum at 30·0°, gave the light yellow liquid 1 : 1 *complex*; this, on cooling, solidified, m. p. 8·5° (Found: C, 17·6; H, 3·6; Nb, 33·6; S, 10·8. NbF_5,Et_2S requires C, 17·3; H, 3·6; Nb, 33·45; S, 11·4%). Since the complex melted at a temperature below that of the experiment, no sharp break was observed in the vapour-pressure–composition curve until it cut the axis at a point corresponding to a 1 : 1 complex. Measurements below the melting point of the complex were impracticable on account of the low vapour pressure of the sulphide. The complex distilled unchanged at about $77°/10^{-3}$ mm.

Tantalum Pentafluoride–Diethyl Sulphide System.—This system behaved like the niobium pentafluoride–diethyl sulphide system; the red liquid, on removal of excess of solvent at 30·0°, gave the light red liquid 1 : 1 *complex* which on cooling solidified to a glass without definite melting point (Found: Ta, 50·0. TaF_5,Et_2S requires Ta, 49·45%). It distilled unchanged at about $80{\cdot}0°/10^{-3}$ mm.

Niobium Pentafluoride–Tetrahydrothiophen System.—Niobium pentafluoride dissolved in tetrahydrothiophen to give a brown solution which, on concentration at 30·0°, deposited a yellow solid; vapour-pressure–composition measurements at 30·0° showed this to be the 1 : 2 *complex* $NbF_5,2(CH_2)_4S$, with a negligible dissociation pressure at this temperature [Found: Nb, 26·05. $NbF_5,2(CH_2)_4S$ requires Nb, 25·55%]. It melted at 60·5° in a vacuum, with some charring; no sublimate was formed.

Tantalum Pentafluoride–Tetrahydrothiophen System.—This system behaved like the last, the yellow 1 : 2 complex melting at 51·0° with decomposition and without the formation of a sublimate in a vacuum.

Niobium Pentafluoride- and Tantalum Pentafluorides–Tetrahydrofuran Systems.—When a quantity of tetrahydrofuran was distilled *in vacuo* on to each of the pentafluorides and the mixtures then allowed to stand for a few minutes at room temperature, the solution became increasingly viscous and turned black. It must be concluded that, as in the parallel experiments with the pentachlorides and pentabromides, the tetrahydrofuran ring is split by these halides, with the formation of polymers.

Replacement Reactions.—*System,* $NbF_5,Et_2O + Et_2S$. An approximately equimolar quantity (2·604 g.) of diethyl sulphide was condensed on to the complex NbF_5,Et_2O (7·192 g.) at $-195°$ in a vacuum apparatus; by contrast with the corresponding pentachloride–diethyl sulphide system, no reaction occurred between the complex and the *gaseous* sulphide. After completion of the condensation, the mixture was allowed to warm to room temperature, where it was found that the ether complex was not miscible with the ethyl sulphide, two layers being formed in the reaction vessel. After standing for 10 min. the volatile fraction was pumped off and condensed, and identified, by refractive index, infrared spectra, vapour pressure, and molecular weight (vapour density), as diethyl sulphide; 2·582 g. (99%) of the sulphide originally added were recovered in this way.

System, $NbF_5,Et_2S + Et_2O$. An approximately equimolar quantity (1·350 g.) of diethyl ether was condensed on to the complex NbF_5,Et_2S (5·066 g.) at −195° in a vacuum apparatus; there was again no reaction between the complex and the gaseous ether. On warming to room temperature, the sulphide complex dissolved completely in the ether. After standing for 10 min. the volatile fraction was pumped off and identified as before, by refractive index, infrared spectra, vapour pressure, and molecular weight (vapour density), as 80% diethyl sulphide.

System, $NbF_5 + Et_2O + Et_2S$. An equimolar mixture of Et_2O (1·015 g.) and Et_2S (1·235 g.) were condensed together in a vacuum on to NbF_5 (2·5735 g.). After warming to room temperature and standing for 10 min., the volatile fraction was pumped off and identified, as before, as Et_2S. The residual liquid was hydrolysed and showed to contain no diethyl sulphide.

DISCUSSION

From these results it may be seen that the two pentafluorides form, with dimethyl ether and dimethyl sulphide, stable crystalline 1 : 1 adducts which are solid at room temperature. Vapour-pressure studies also indicate the formation, with these ligands, of 1 : 2 adducts which possess high dissociation pressures at room temperature and were not isolated. The dissociation pressures of all the 1 : 1 adducts are small and the adducts can be distilled at *ca.* 10^{-3} mm. with only a small amount of decomposition into their components, the gas disengaged in each case being identified, from its mass spectrum, as the unchanged ligand; in a closed system at this pressure they can be distilled completely. The dimethyl sulphide complexes, in addition, sublime unchanged in a closed system at low pressures, at temperatures below their melting points. The 1 : 1 adducts of these pentafluorides with diethyl ether and diethyl sulphide, on the other hand, are liquid at room temperature and likewise can be distilled unchanged at low pressures. Tetrahydrothiophen forms 1 : 2 complexes which melt with decomposition at 60·5 and 51·5°, respectively. The ring of tetrahydrofuran, on the other hand, is broken, with charring and the formation of polymeric products.

The replacement reactions described above showed that Et_2S could not displace any Et_2O from NbF_5,Et_2O, but that Et_2O could displace most of the Et_2S from NbF_5,Et_2S. This is in contrast to the experiments with the corresponding pentachloride complexes with these ligands, in which it was observed that Et_2S reacted exothermically with $NbCl_5,Et_2O$ with complete displacement of the ether. A similar result was obtained with the di-n-propyl ether and disulphide complexes of niobium pentachloride, although neither Me_2S nor Me_2O displaced the other from their complexes with niobium or tantalum pentachloride.[11] The present experiments with the niobium pentafluoride complexes are not strictly comparable with the foregoing, since NbF_5,Et_2O is insoluble, or nearly so, in Et_2S whilst both the complexes and the parent pentafluoride are polymerised to different degrees.

Further information about the pentafluoride complexes, especially as regards their polymerisation and ionic dissociation, was sought through a study of the densities, viscosities, and electrical conductivities of the diethyl ether and diethyl sulphide complexes with niobium and tantalum pentafluorides. These are given in Table 1, and Table 2 includes the energy of activation of molar conductance (E_μ), the energy of activation of viscous flow (E_η), and the constants b and B in the Batschinski equation, $v = b + B\phi$, where v is the specific volume, ϕ the fluidity (η^{-1}), and B is proportional to the size of the flow unit. A number of conclusions may be drawn from these figures. In the first place, the viscosities of the complexes are less than those of the parent pentafluorides whilst the sulphide complexes are more viscous than the corresponding ether complexes: this is especially marked in the case of the niobium pentafluoride complexes. These comparisons suggest a greater degree of association in the sulphide complexes, which is supported by

TABLE 1.

Densities, viscosities, and electrical conductivities.

	NbF_5,Et_2O					NbF_5,Et_2S			
t (°c)	$\kappa \times 10^4$ (ohm^{-1} cm.$^{-1}$)	η (cp.)	d_4^t (g. cm.$^{-3}$)	$\mu \times 10$ (ohm^{-1} cm.^{2} mole^{-1})	t (°c)	$\kappa \times 10^3$ (ohm^{-1} cm.$^{-1}$)	η (cp.)	d_4^t (g. cm.$^{-3}$)	$\mu \times 10$ (ohm^{-1} cm.^{2} mole^{-1})
20·0	5·908	3·424	1·7046	0·9082	20·0	1·718	28·97	1·7871	2·673
25·0	6·541	3·063	1·6971	1·010	25·0	2·107	22·01	1·7777	3·296
30·0	7·254	2·744	1·6897	1·125	30·0	2·570	17·00	1·7684	4·041
35·0	8·006	2·471	1·6823	1·247	35·0	3·112	13·18	1·7590	4·920
40·0	8·789	2·230	1·6749	1·375	40·0	3·726	10·59	1·7496	5·923
45·0	9·635	2·016	1·6675	1·514	45·0	4·461	8·143	1·7402	7·129

$d_4^t = 1\cdot7342 - 1\cdot482 \times 10^{-3}t$. $d_4^t = 1\cdot8246 - 1\cdot875 \times 10^{-3}t$.

	TaF_5,Et_2O					TaF_5,Et_2S			
20·0	10·12	4·397	2·2569	1·570	20·0	2·465	11·89	2·2683	3·979
25·0	11·23	3·890	2·2470	1·750	25·0	2·837	9·539	2·2566	4·603
30·0	12·44	3·454	2·2371	1·947	30·0	3·254	7·729	2·2437	5·309
35·0	13·77	3·078	2·2272	2·164	35·0	3·715	6·288	2·2314	6·095
40·0	15·11	2·754	2·2173	2·386	40·0	4·218	5·177	2·2191	6·958
45·0	16·57	2·492	2·2074	2·627	45·0	4·772	4·284	1·9412	7·916

$d_4^t = 2\cdot2965 - 1\cdot980 \times 10^{-3}t$. $d_4^t = 2\cdot3175 - 2\cdot460 \times 10^{-3}t$.

TABLE 2.

	NbF_5,Et_2O	TaF_5,Et_2O	NbF_5,Et_2S	TaF_5,Et_2S
$E\eta$ (kcal. mole^{-1})	3·891	4·236	9·374	7·584
$E\mu$ (kcal. mole^{-1})	3·786	3·817	7·259	5·104
$E\eta/E\mu$	1·03	1·11	1·29	1·48
$\mu\eta$ (cm.^{2} cp. ohm^{-1} mole^{-1})	0·308	0·680	7·25	4·39
b (cm.^{2} g.$^{-1}$)	0·586	0·428	0·554	0·433
B (cm.^{2} cp. g.$^{-1}$)	0·0644	0·0641	0·185	0·121

the much higher values of B in the Batschinski equation.[12] The ratio of the values of E_μ and E_η in the case of each of the complexes approaches unity, which enables a rough estimate to be made, from the magnitude of $\mu\eta$, of the percentage of ionisation in the melts.[13] Moreover, the values of E_μ and E_η fall within the range 3—8 kcal. mole^{-1}, similar to those of boron trifluoride and gallium trichloride complexes.[13] The ionisation in the latter case also varies from about 0·5 to 7%.

The greater degree of ionisation of the present sulphide complexes, as compared with their ether analogues, is doubtless connected in part with their greater degree of polymerisation which allows the ionic charge to be spread. As to the actual nature of the ions, no definite conclusion can be drawn at this stage.

Information regarding the nature of complexes can sometimes be gained from a consideration of the molar volumes of the components and of the complex, and the extent by which the latter differs from the sum of the former. In Table 3 are given the molar volumes at 25° (V_M^{25}) of the uncomplexed components, their sums, the molar volumes of the complexes, and the diminution of volume on formation of the complex. It may be

TABLE 3.

Molar volumes of the complexes and their components.

V_M^{25} (c.c.): NbF_5, 69·71; TaF_5, 71·10; Et_2O, 104·74; Et_2S, 108·41.

$NbF_5 + Et_2O$	174·45	$NbF_5 + Et_2S$	178·12	$TaF_5 + Et_2O$	175·84	$TaF_5 + Et_2S$	179·51
NbF_5,Et_2O	154·40	NbF_5,Et_2S	156·43	TaF_5,Et_2O	155·76	TaF_5,Et_2S	162·26
$-\Delta V_M$	20·05		21·69		20·08		17·25

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[12] Batschinski, *Z. phys. Chem.*, 1913, **84**, 643.

[13] Greenwood, *J.*, 1953, 1427; Greenwood and Martin, *J.*, 1953, 4132; Greenwood and Wade, *J.*, 1957, 1516.

seen that the contraction in total molar volume on formation of the complexes varies between about 10 and 12%. No clear trend is apparent, and further work, with other complexes, is necessary before any conclusions can be drawn from such considerations regarding the relative lengths of the metal–oxygen and metal–sulphur bonds.

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