Reactions of Niobium and Tantalum Pentafluorides with Trimethylsilyldiethylamine and with Trimethylsilyl Chloride

By **J. C. Fuggle, D. W. A. Sharp,** and **J. M. Winfield,*** Chemistry Department, University of Glasgow, Glasgow

The diethylamido-niobium and -tantalum fluorides, MF_4NEt_2 and $MF_3(NEt_2)_2$ are formed from the pentafluorides and Me_3SiNEt_2 at 20 °C. They are weaker Lewis acids than the pentafluorides and are thought to be fluoro-bridged polymers from their i.r. spectra. Niobium pentafluoride reacts with Me_3SiCl in Et_2O to give labile niobium chlorofluoride species and finally $NbCl_5,OEt_2$.

The only substituted derivatives of niobium and tantalum pentafluorides that have been investigated to any extent are the chlorofluorides, which are prepared from PCl_5,MCl_5 (M = Nb or Ta), and AsF_3.[1] They reorganise rapidly in acetonitrile to give $MCl_5,NCMe$ and $MF_5,NCMe$, and only the tetrachloride, fluorides are well characterised. MCl_4F have tetrameric fluoro-bridged structures[2] similar to that of the pentafluorides.[3] In this paper we describe the preparation of previously unreported diethylamido-derivatives of NbF_5 and TaF_5 from reactions of the fluorides with trimethylsilyldiethylamine. Analogous reactions of NbF_5 with trimethylsilyl chloride are described also. Dialkylamido-derivatives of non-metal fluorides,[4] tungsten hexafluoride,[5] titanium tetrachloride, and tetrabromide,[6] have been prepared previously using silylamines, and tungsten(VI) chlorofluorides have been observed in the reaction of WF_6 and Me_3SiCl.[7]

RESULTS

Reactions of Niobium and Tantalum Pentafluorides with Trimethylsilyldiethylamine.—Mono- and bis-diethylamido-niobium(V) and -tantalum(V) fluorides are prepared conveniently from $(MF_5)_4$ or MF_5,OEt_2 and Me_3SiNEt_2 at 20 °C. The compounds MF_4NEt_2 are formed from reactions employing a small excess of MF_5,OEt_2, while $MF_3(NEt_2)_2$ are the products from dry reactions between $(MF_5)_4$ and a large excess of Me_3SiNEt_2. In all cases the other product is Me_3SiF. The formation of more highly substituted products and those of intermediate composition was not observed under the conditions used. The diethylamido-derivatives (Table 1) are rapidly hydrolysed in moist air, involatile at 20 °C, melt without apparent decomposition, and are almost insoluble in Et_2O and other organic solvents. Their colours presumably arise from $M \longleftarrow NEt_2$ charge transfer. They form 1 : 1 complexes with pyridine or 4-methylpyridine but no isolable complexes are formed with MeCN or Et_2O. Apparently they are weaker Lewis acids than the pentafluorides as $MF_5(py)_2$ and MF_5L, L = MeCN or Et_2O, are well known.[8]

TABLE 1

Diethylamino niobium and tantalum fluorides

			Analysis									
			Found (%)					Required (%)				
Compound	Colour	M.p. (°C)	C	H	F	N	M	C	H	F	N	M
NbF_4NEt_2	Orange	150	19·8	4·3	31·2	5·9	37·8	19·9	4·2	31·5	5·8	38·6
TaF_4NEt_2	Pale yellow	123	14·7	3·7	22·5	4·2	54·8	14·6	3·1	23·1	4·3	55·0
$NbF_3(NEt_2)_2$	Scarlet	82	32·2	6·8	19·8	9·4	31·1	32·7	6·9	19·4	9·5	31·6
$TaF_3(NEt_2)_2$	Yellow	203	24·4	5·2	14·9	7·6	48·1	25·1	5·3	14·9	7·3	47·3
TaF_4NEt_2,py	Yellow	115	26·0	3·6	19·1	6·7	44·9	26·5	3·7	18·6	6·9	44·3
TaF_4NEt_2,4-Mepy	Yellow	122	28·7	3·4	18·4	6·7		28·5	4·0	18·0	6·6	
$NbF_3(NEt_2)_2,py$	Brown	56	41·7	6·8	14·8	11·3	24·5	41·8	6·9	15·3	11·3	24·9
$TaF_3(NEt_2)_2,py$	Brown	51	32·9	5·3	12·7	9·2	39·9	33·8	5·5	12·4	9·1	39·2
$TaF_3(NEt_2)_2$,4-Mepy	Pale brown	Liquid	35·9	5·5	11·5	9·0	37·9	35·4	5·7	12·0	8·8	38·1

The i.r. spectra of MF_4NEt_2 and $MF_3(NEt_2)_2$ contain series of strong bands in the region 1200—890 cm^{-1} which are attributed to the $-NEt_2$ groups by analogy with the spectra of transition metal dialkylamides.[9] The main features in the 800—250 cm^{-1} region are a set of partially resolved bands *ca.* 700—580 cm^{-1} and a broad, strong band at 480 [NbF_4NEt_2], 458 [$NbF_3(NEt_2)_2$], 499 [TaF_4NEt_2], and 475 cm^{-1} [$TaF_3(NEt_2)_2$]. These latter bands may be compared with bands in the i.r. spectra of $(NbF_5)_4$ and $(TaF_5)_4$ at 498 and 511 cm^{-1} respectively, and with bands at 485 and 495 cm^{-1} in $(NbCl_4F)_4$ and $(TaCl_4F)_4$, which have been assigned to stretching modes involving the M–F–M bridges.[10] Similar bands are not observed for the pyridine and 4-methylpyridine complexes although their i.r. spectra in the 1200—890 cm^{-1} region are similar to MF_4NEt_2 and $MF_3(NEt_2)_2$. We suggest that the bands observed in the spectra of

---

[1] L. Kolditz and U. Calov, *Z. anorg. Chem.*, 1970, **376**, 1.

[2] H. Preiss, *Z. anorg. Chem.*, 1966, **346**, 272; 1968, **362**, 13.

[3] A. J. Edwards, *J. Chem. Soc.*, 1964, 3714.

[4] *E.g.*, R. Schmutzler, *Angew. Chem.*, 1964, **76**, 893; G. C. Demitras and A. G. MacDiarmid, *Inorg. Chem.*, 1967, **6**, 1903.

[5] A. Majid, R. R. McLean, D. W. A. Sharp, and J. M. Winfield, *Z. anorg. Chem.*, 1971, **385**, 85.

[6] H. Bürger and H.-J. Neese, *Z. anorg. Chem.*, 1969, **365**, 243; 1969, **370**, 275.

[7] G. W. Fraser, C. J. W. Gibbs, and R. D. Peacock, *J. Chem. Soc.* (*A*), 1970, 1708.

[8] (*a*) H. C. Clark and H. J. Emeléus, *J. Chem. Soc.*, 1958, 190; (*b*) K. C. Moss, *J. Chem. Soc.* (*A*), 1969, 1224; (*c*) J. A. S. Howell and K. C. Moss, *ibid.*, 1971, 2483; (*d*) J. C. Fuggle, D. W. A. Sharp, and J. M. Winfield, *J. Fluorine Chem.*, 1972, **1**, 427.

[9] (*a*) H. Bürger, H. Stammreich, and Th. T. Sans, *Monatsh.*, 1966, **97**, 1276; (*b*) D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc.* (*A*), 1969, 980.

[10] H. Preiss and P. Reich, *Z. anorg. Chem.*, 1968, **362**, 19; I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc.* (*A*), 1969, 958.

MF_4NEt_2 and $MF_3(NEt_2)_2$ *ca.* 700—580 cm^{-1} are due to M–F(terminal) and M–NEt_2 groups and that these compounds have polymeric, fluoro-bridged structures in the solid state.

Reactions of Niobium Pentafluoride with Trimethylsilyl Chloride.—The behaviour of NbF_5 towards Me_3SiCl is more complicated than that with Me_3SiNEt_2. Although Nb–F bonds are replaced by Nb–Cl bonds, as evidenced by the formation of Me_3SiF, discrete niobium chlorofluorides were not isolated. The ^{19}F n.m.r. spectrum of a solution whose composition is $NbF_5 : Me_3SiCl : Et_2O = 1 : 2{\cdot}2 : 1$ indicates that more than one Nb–F species is present, but gives no stereochemical information. Other reactions of Me_3SiCl with NbF_5 in Et_2O are summarised in Table 2. $NbCl_5,OEt_2$ is obtained from solution when the mole ratio $Me_3SiCl : NbF_5 = 5 : 1$. Although the reduction of $NbCl_5$ by pyridine to give $NbCl_4py$ has been reported,[11] $NbCl_5py$ can be prepared from $NbCl_5,OEt_2$ providing excess of pyridine is removed quickly from the product, and apparently is stable indefinitely in the absence of excess of pyridine. Addition of pyridine to ether solutions in which the mole ratio $Me_3SiCl : NbF_5$ is 1 : 2, 1 : 1, or 2 : 1 precipitates yellow solids which have sharp m.p.s and whose analyses correspond to $Nb_2ClF_9py_4$, $NbClF_4py_2$, and $NbCl_2F_3py$ respectively. Their i.r. and Raman spectra and *X*-ray powder data differ from each other and from those of NbF_5py_2 and $NbCl_5py$, but do not provide sufficient evidence to state that the compounds are discrete.

TABLE 2

Reactions of NbF_5 with Me_3SiCl

Reactants (mmol)					Analysis											
					Found (%)						Required (%)					
NbF_5	Me_3SiCl	Et_2O	Product [a]	M.p. (°C)	C	H	Cl	F	N	Nb	C	H	Cl	F	N	Nb
13·8	6·9	21·6	$Nb_2ClF_9py_4$	166	32·9	3·4	4·8	24·4	7·7		33·9	2·9	5·0	24·1	7·9	
6·7	6·7	33·0	$NbClF_4py_2$	148	33·0	3·0	10·0	20·7	7·8		33·1	2·8	9·8	21·0	7·7	
7·2	14·5	22·3	$NbCl_2F_3py_2$	126 (decomp.)	31·7	3·0	18·4	14·9	7·4	24·5	31·7	2·7	18·7	15·0	7·4	24·5
7·8	41·9	33·3	$NbCl_5,OEt_2$ [b]	80	13·9	3·1	51·7			26·5	13·9	2·9	51·5			27·0

[a] Pyridine was added sufficient to precipitate the Nb containing species. [b] In the absence of pyridine. Addition of pyridine to a small quantity of $NbCl_5,OEt_2$ gave $NbCl_5py$ m.p. 220 °C (decomp.). Found C, 17·6; H, 1·7; Cl, 50·0; N, 3·9; Nb, 26·7%. $C_5H_5Cl_5NNb$ requires C, 17·2; H, 1·4; Cl, 50·8; N, 4·0; Nb, 26·6%.

DISCUSSION

These reactions may be rationalised in the following way. In Et_2O solution niobium and tantalum pentafluorides are present as MF_5,OEt_2 which are believed to be monomeric.[8b,c] NbF_5,OEt_2 reacts with Me_3SiCl, presumably by a process involving nucleophilic attack at Nb by the Si–Cl group as no reaction occurs between NbF_5 and $SiCl_4$,[12] to give NbF_4Cl,OEt_2 or more highly substituted compounds and Me_3SiF. By analogy with $MF_{6-n}Cl_n^-$ (M = Nb or Ta), anions,[13] and $WF_{6-n}Cl_n$,[7] redistribution reactions giving other members of the series $NbF_{5-n}Cl_n,OEt_2$ are expected to occur. Thus a solution will contain several species whose concentrations will depend on the mole ratio $Me_3SiCl : NbF_5$. Addition of pyridine displaces Et_2O and the least soluble species are precipitated, but it cannot be assumed that the distributions of fluoro- and chloro-ligands about niobium are identical in the solution and solid species.

MF_4NEt_2 are formed readily from MF_5,OEt_2 and Me_3SiNEt_2 but because of their relatively weak Lewis acidity and insolubility in Et_2O, further substitution is very slow. Attempts to prepare $Nb(NEt_2)_5$ from $NbCl_5$ and $LiNEt_2$ result in the formation of $Nb(NEt_2)_4$, and although $Ta(NEt_2)_5$ is formed in an analogous reaction it is easily decomposed to $EtN{:}Ta(NEt_2)_3$ and $Ta(NEt_2)_4$.[14] Although $WF_2(NEt_2)_4$ has been prepared from WF_6 and Me_3SiNEt_2,[15] the formation of polymeric niobium and tantalum fluorides having more than two $-NEt_2$ substituents could be sterically unfavourable.

Spectroscopic [9b] and structural [16] evidence suggests that dialkylamido-ligands are good π-donors to d^0 transition metals. The weak Lewis acid properties of MF_4NEt_2 and $MF_3(NEt_2)_2$ relative to MF_5 may be understood on this basis. It is considered that the lack of reaction between $MF_3(NEt_2)_2$ and Me_3SiNEt_2 is determined both by electronic and by steric factors.

EXPERIMENTAL

All operations were carried out *in vacuo* or in a Lintott inert atmosphere box in which the concentrations of H_2O and O_2 were $\leqslant 12$ p.p.m. I.r. spectra were obtained using a Perkin-Elmer 457 spectrometer, the samples being mounted as Nujol of Fluorube mulls between AgCl, KBr, Si, and Ge windows. To prevent reactions between the fluorides and Nujol, the latter was purified by prolonged shaking with H_2SO_4 followed by several distillations from Na metal. Raman spectra were obtained using a Cary 81 spectrometer with He–Ne excitation (University of Strathclyde), the solid samples being sealed in 5 mm Pyrex tubes with optically flat ends. N.m.r. spectra were recorded using a Perkin-Elmer R10 instrument at 60·0 MHz (^1H) and 56·4 MHz (^{19}F) with a probe temperature of 33°. Niobium and Tantalum were determined gravimetrically as M_2O_5 and microanalyses were by Beller or Bernhardt laboratories.

[11] M. Allbutt, K. Feenan, and G. W. A. Fowles, *J. Less-Common Metals*, 1964, **6**, 299; J. O'Keane, Ph.D. Thesis, University of Glasgow, 1971.

[12] J. H. Canterford and T. A. O'Donnell, *Inorg. Chem.*, 1966, **5**, 1442.

[13] Yu. A. Buslaev, E. G. Ilin, S. V. Bainova, and M. N. Krutkina, *Doklady Akad. Nauk S.S.S.R.*, 1971, **196**, 374.

[14] D. C. Bradley and I. M. Thomas, *Canad. J. Chem.*, 1962, **40**, 449, 1355.

[15] A. Majid, D. W. A. Sharp, and J. M. Winfield, unpublished work.

[16] *E.g.*, D. C. Bradley, M. H. Chisholm, C. E. Heath, and M. B. Hursthouse, *Chem. Comm.*, 1969, 1261; C. E. Heath and M. B. Hursthouse, *ibid.*, 1971, 143.

Niobium and tantalum pentafluorides, prepared from the metals and fluorine at 300 °C, were purified by repeated sublimation. Trimethylsilyldiethylamine was prepared from trimethylsilyl chloride and $NHEt_2$ *in vacuo*, and was freed from NH_2Et_2Cl by repeated vacuum distillation. Me_3SiCl (Fluka, *puriss.*) was dried over 3 Å molecular sieves and organic solvents were dried by standard methods. Reactions between MF_5 and Me_3SiX, $X = NEt_2$ or Cl, were carried out *in vacuo* in a two compartment vessel designed to enable precipitated solids to be washed with solvent.

Reactions with Me_3SiNEt_2.—(*a*) NbF_5 (11·7 mmol), Me_3SiNEt_2 (11·3 mmol) and Et_2O (24·2 mmol) gave an orange solution which was shaken for 2 h to give Me_3SiF, identified by i.r. spectroscopy,[17] and an orange precipitate. Me_3SiF and a yellow precipitate were obtained from TaF_5 (18·4 mmol), Me_3SiNEt_2 (13·2 mmol), and Et_2O (62·3 mmol) under similar conditions. The solid products were identified as *diethylamidoniobium*(V) *tetrafluoride* and *diethylamidotantalum*(V) *tetrafluoride* respectively (Table 1). Their *X*-ray powder data [18] indicated that $(MF_5)_4$ was absent. I.r. and Raman spectra (1200—200 cm^{-1}) were as follows: NbF_4NEt_2 i.r. 1189m, 1124s, 1092ms, 1069ms, 1035ms, 994s, 907sh, 901sasy, 793ms, 722w, 674w, 646vsbr, 622w, 600vs, 595w, 480sbr, 325ms cm^{-1}; Raman 1187(15), 1071(7), 1033(7), 994(30), 898(40), 790(8), 638(15), 594(28), 334(25) cm^{-1}; TaF_4NEt_2 i.r. 1192ms, 1126m, 1093ms, 1071m, 1043ms, 1004s, 917ms, 905w, 794ms, 723mw, 666s, 638vs, 620vs, 550w, 499sbr, 420w, 365mbr, 306m, 240s cm^{-1}; Raman 1003(15), 919(2), 662(28), 598(18), 305(10) cm^{-1}.

(*b*) Mixtures of the pentafluorides and a large excess of Me_3SiNEt_2 were shaken at 20 °C. Viscous liquids were formed after 8 h; further reaction gave scarlet or yellow solids after 3 days. Me_3SiF and unchanged Me_3SiNEt_2 were removed, the solids were crushed in the inert atmosphere box, and were shaken for a further 3 days with Me_3SiNEt_2. The solid products isolated after this time were identified as *bis*(*diethylamido*)*niobium*(V) *trifluoride* and *bis*(*diethylamido*)*tantalum*(V) *trifluoride* (Table 1). Their *X*-ray powder data [18] indicated that $(MF_5)_4$ and MF_4NEt_2 were absent. I.r. spectra (1200—200 cm^{-1}) were as follows: $NbF_3(NEt_2)_2$ i.r. 1190ms, 1136s, 1090ms, 1068ms, 1050ms, 1000vsasy, 906sh, 890vs, 843w, 790s, 723w, 630vs, 610w, 584vs, 458vsbr, 330sh, 320ms, 306sh cm^{-1}; $TaF_3(NEt_2)_2$ i.r. 1191s, 1142 1136s, 1094s, 1066w, 1052ms, 1018m, 1002s, 904w, 894s, 789s, 723m, 662w, 610vsbr, 595sh, 523w, 475vsbr, 292msbr cm^{-1}. Satisfactory Raman spectra of these compounds could not be obtained.

(*c*) Pyridine and 4-methylpyridine complexes (Table 1) of the diethylamido-metal fluorides were obtained by direct combination using excess of the ligand. I.r. and *X*-ray powder data are reported elsewhere,[18] but the i.r. spectrum (1200—200 cm^{-1}) of TaF_4NEt_2py was typical of those obtained: 1193m, 1159w, 1130m, 1095mw, 1069s, 1049s, 1008sbr, 956w, 906s, 792m, 762s, 697s, 681w, 644s, 631w, 590vs, 580vs, 450w, 433w, 336m, 310mbr, 262m, 240s cm^{-1}.

Reactions with Me_3SiCl.—Me_3SiCl (6·8 mmol) and NbF_5 (3·2 mmol) at 20 °C gave Me_3SiF and a yellow solid from which a viscous yellow liquid was distilled at 140 °C. This was not investigated further. Other reactions (Table 2) were performed in Et_2O, using pyridine to precipitate solid products. The vibrational spectra and *X*-ray powder data of these products are reported elsewhere.[18]

[2/826 *Received*, 12*th April*, 1972]

---

[17] H. Kriegsmann, *Z. anorg. Chem.*, 1958, **294**, 113.
[18] J. C. Fuggle, Ph.D. Thesis, University of Glasgow, 1971.