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NIOBIUM, TANTALUM AND MOLYBDENUM PENTAFLUORIDE COMPLEXES WITH ORGANIC LIGANDS

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SUMMARY

The following new transition metal pentafluoride complexes with organic ligands have been prepared: MF_5L (M = Nb or Ta, L = Me_2SO, EtCN, or CH_2ClCN) (nc), TaF_5(2-Me-py) (nc), MoF_5L (L = MeCN or CH_2ClCN) (nc) and TaF_5(4-Me-py)$_2$ (nc). Their vibrational spectra and those of MF_5NCMe (M = Nb or Ta) and MF_5L_2 (M = Nb or Ta, L = Me_2SO or py) are discussed in terms of the previously proposed structures, monomeric MF_5L and $[MF_4L_4^+]$ $[MF_6^-]$.

INTRODUCTION

The 1:1 and 1:2 complexes formed between niobium, tantalum, or molybdenum pentafluorides and organic ligands are of interest in view of the tetrameric, fluoro-bridged structures adopted by the parent molecules[1]. We report the preparation of new complexes of this type and the results from an examination of the vibrational spectra of these and related complexes, which was undertaken to obtain information on their structures in the solid state. Electrical conductivity and viscosity measurements on $MF_5 \cdot XEt_2$ (M = Nb or Ta, X = O or S) and $MF_5(OSMe_2)_2$ (M = Nb or Ta) in the molten state suggest some degree of polymerisation and ionisation, particularly for the dimethyl sulphoxide complexes[2,3]. NMR spectra due to the NbF_6^- anion have been observed from a solution of NbF_5 in dimethylformamide[4]. A recent NMR and IR spectroscopic study, reported while the present work was in progress, has suggested that 1:2 NbF_5 complexes have the structure $[NbF_4L_4^+]$ $[NbF_6^-]$ (L = py, Me_2SO, or Me_2NCHO) and that 1:1 complexes are probably monomeric NbF_5L (L = MeCN, Et_2O or Et_2S) in solution[5]. Similar structures are suggested for TaF_5 complexes[6].

EXPERIMENTAL

All operations were carried out under vacuum or in a Lintott inert atmosphere box in which the concentrations of H_2O and O_2 were < 12 ppm. Niobium and tantalum pentafluorides, prepared from the metals and fluorine at 300°, and molybdenum pentafluoride, prepared by the reduction of the hexafluoride with molybdenum metal at 140°, were purified by repeated sublimation. The organic ligands were commercial products, which were rigorously purified and dried by standard procedures, and stored over Na or 5A molecular sieves.

Preparation of the 1:2 dimethyl sulphoxide complexes by the reported procedure[3] gave impure products. Some volatile material was observed, suggesting that fluorination of Me_2SO with equivalent formation of metal oxofluorides had occurred. Analytically pure products were obtained by the addition of Me_2SO to solutions of $MF_5{\bullet}OEt_2$ ($M = Nb$ or Ta) in diethyl ether at 20°. With the mole ratio $MF_5:Me_2SO \leqslant 1:1$, complexes of 1:1 stoichiometry were precipitated and with a mole ratio of $\geqslant 1:2$, 1:2 complexes were obtained. The X-ray powder photographs of the products indicated that distinct phases were obtained in each case, and their melting points were as follows: 1:1 complexes 125° (Nb), 133° (Ta); 1:2 complexes 55–64° (Nb), 79° (Ta). The remaining complexes were prepared by direct mixing of the components below 20°, followed by removal of excess ligand. Microanalyses (Table 1) were by Laboratorium Beller, Göttingen.

IR spectra were obtained using a Perkin–Elmer 457 spectrometer, the samples being mounted as Nujol mulls between AgCl, KBr, Si or Ge windows. To prevent reactions between the complexes and Nujol, the latter was purified by prolonged shaking with H_2SO_4, followed by several distillations from Na. Raman spectra were obtained using a Cary 81 spectrometer with He/Ne laser excitation (University of Strathclyde), the solid samples being sealed in 5 mm Pyrex tubes with optically flat ends.

RESULTS AND DISCUSSION

Details of the complexes prepared are given in Tables 1–3. 1:1 Complexes of niobium or tantalum pentafluoride with dimethyl sulphoxide, the propionitrile and chloroacetonitrile complexes, and the 1:1 complex of molybdenum pentafluoride with acetonitrile, have not been reported previously. The latter complex is distinct from $MoF_5(NCMe)_2$[7].

All the compounds studied are white or colourless, although impure samples are yellow, brown or violet. In some cases, analytically pure products could not be obtained, possibly due to reduction of the pentafluoride by the organic ligand. Thus NbF_5 with 2-methyl-, or 4-methyl-pyridine gives coloured products, whereas TaF_5(2-Me-py) and $TaF_5(\text{4-Me-py})_2$ are readily isolated. The different stoichiometries probably reflect the steric requirements of the ligands, but it appears that

TABLE 1

ANALYTICAL DATA

	C%		H%		F%		N%		Cl or S%	
	req.	found	req.	found	req.	found	req.	found	req.	found
NbF_5•NCMe	10.5	10.4	1.3	1.4	41.5	41.0	6.1	6.0		
TaF_5•NCNe	7.6	7.3	1.0	1.5	30.0	30.4	4.4	4.3		
MoF_5•NCMe[a]	10.4	10.5	1.3	1.4	40.9	39.7	6.0	5.9		
NbF_5•NCEt[a]	14.8	14.7	2.1	2.3	39.1	38.7	5.8	5.7		
TaF_5•NCEt[a]	10.9	10.4	1.5	2.2	28.7	28.9	4.2	3.9		
NbF_5•$NCCH_2Cl$[a]	9.1	8.5	0.8	1.1	36.1	36.1	5.3	4.8	13.5	12.5
TaF_5•$NCCH_2Cl$[a]	6.8	6.5	0.6	1.5	27.0	27.2	4.0	3.6	10.1	9.5
MoF_5•$NCCH_2Cl$[a]	9.0	9.3	0.8	0.9	35.6	34.5	5.3	5.4	13.3	13.6
NbF_5•$OSMe_2$[a]	9.0	9.1	2.3	2.4	35.7	35.2			12.1	12.1
TaF_5•$OSMe_2$[a]	6.8	6.8	1.7	1.8	26.8	27.6			9.1	9.0
$NbF_5(OSMe_2)_2$	14.0	14.0	3.5	3.7	27.6	27.2			18.6	17.8
$TaF_5(OSMe_2)_2$	11.1	11.0	2.8	2.9	22.0	22.0			14.8	14.7
NbF_5py_2	34.7	34.6	2.9	3.3	27.5	27.7	8.1	8.1		
TaF_5py_2	27.7	27.4	2.3	1.9	21.9	22.2	6.5	6.4		
TaF_5(2-Me-py)[a]	19.5	20.1	1.9	2.1	25.7	25.0	3.8	3.9		
$TaF_5(4\text{-Me-py})_2$[a]	31.1	29.5	3.1	3.0	20.5	20.7	6.1	6.2		

[a] Not previously reported.

TABLE 2

BANDS ATTRIBUTED TO METAL–FLUORIDE MODES IN THE VIBRATIONAL SPECTRA ($800–300\ cm^{-1}$) OF 1:1 PENTAFLUORIDE:LIGAND COMPLEXES

	Ta		Nb		Mo	
Ligand	IR	Raman	IR	Raman	IR	Raman
Me_2SO	722 m		721 m–w			
	677 m	673 (15)	664 m–s	665 (15)		
	572 s, asym		625 vs			
			605 vs			
MeCN	712 vs	710 (30)	710 s	702 (30)	703 m–w	697 (90)
	655 m		660 s	673 (3)	650 vs	665 (5)
	612 s		638 s		635 sh	
				592 (2)		
EtCN	708 s	not obtained	710 s	702 (200)		
	657 sh		666 s	668 sh		
	615 vs		638 s			
				596 (10)		
CH_2ClCN	715 s	712 (40)	719 s	714 (12)	710 m	706 (200)
	669 m–s	673 (30)	660 vs	684 (14)	660 s	679 } (15)
	630 m		625 vs		630 s	670 }
	608 vs	609 (15)				
2-Me-py	698 s	not obtained				
	609 vs					
	590 sh					

w = weak, m = medium, s = strong, sh = shoulder, asym = asymmetric, Raman intensities in parentheses.

TABLE 3

BANDS ATTRIBUTED TO METAL–FLUORIDE MODES IN THE VIBRATIONAL SPECTRA (700–300 cm^{-1}) OF 1:2 PENTAFLUORIDE:LIGAND COMPLEXES

$NbF_5(OSMe_2)_2$	IR[a]	635 sh, 616 sh, 603 s, 579 m, 555 m, 452 m, 408 s, 358 m[b], 330 m[b]
$TaF_5(OSMe_2)_2$	IR[a]	583 s, asym, 570 w, 550 vs, 472 m, 460 sh, 359 m[b], 330 m[b]
NbF_5py_2	IR	614 s, asym, 602 s, 584 w, 563 s, 343 m
	Raman	687(100), 676(55), 640(55), 588(40)
TaF_5py_2	IR	585 vs, 330 m
	Raman	693(40), 645(45), 603(60), 320 w
$TaF_5(4\text{-Me-py})_2$	IR	584 vs, 578 vs, 332 m–s
	Raman	687(40)[b], 670(50)[b], 613(90), $\sim$300(8)

w = weak, m = medium, s = strong, sh = shoulder, asym = asymmetric, Raman intensities in parentheses.

[a] No peaks definitely attributable to M–F modes were observed in the Raman spectrum.

[b] One of these peaks is probably due to a ligand vibration.

when the steric requirements of the ligand are not great, both 1:1 and 1:2 complexes may be prepared.

It was not feasible to obtain a complete vibrational spectrum of any one complex. They are weak Raman scatterers, characteristically give rise to broad IR bands, and are too reactive to obtain satisfactory IR spectra below 250 cm^{-1}. In examining a wide range of compounds, a partial interpretation of the spectra is possible by comparison with the spectra of the ligands and the pentafluorides, supplemented in the case of the dimethyl sulphoxide and pyridine complexes by deuteriation studies.

The spectra of the 1:2 complexes indicate that both ligands are coordinated. Bands assigned to predominantly S–O stretching modes in the 1:2 Me_2SO complexes are at 966 and 935 cm^{-1} (Nb), and at 970 and 938 cm^{-1} (Ta), suggesting that the Me_2SO ligands occupy non-equivalent environments. Corresponding vibrations in the 1:1 complexes occur at 955 cm^{-1} (Nb) and 963 cm^{-1} (Ta). Metal–oxygen stretching modes occur in the region 470–450 cm^{-1} and in the other complexes it is considered that metal–ligand modes will occur below 300 cm^{-1}.

Bands which are assigned to predominantly metal–fluoride stretching modes are given in Tables 2 and 3. The major difference in this region between the complexes and the pentafluorides themselves is that the IR spectra of the latter contain a strong band at *ca.* 500 cm^{-1}. A vibrational analysis of $(NbF_5)_4$ has indicated that stretching modes of the Nb–F–Nb bridges occur in this region [8], and similar bands are present in the IR spectra[9] of niobium and tantalum tetrachloride fluorides, which have fluoro-bridged structures similar to the pentafluorides[10]. The absence of such bands in the complexes suggests that they are not fluoro-bridged polymers.

If the 1:1 complexes are monomeric with C_{4v} symmetry, four metal–fluoride stretching vibrations, $2a_1$ (Raman, IR) + b_1 (Raman) + e (Raman, IR) are expected. For a lower symmetry, the b_1 mode becomes Raman active and the e modes non-degenerate, a situation which has been observed in solid tungsten chloride pentafluoride[11]. From a comparison of the data in Table 2 with the spectrum of solid $WClF_5$, we suggest that the 1:1 complexes are monomeric in the solid state with a site symmetry lower than C_{4v}.

For the 1:2 complexes the presence of a strong, IR active band in the region 580–610 cm^{-1}, assigned to the ν_3 mode of an octahedral MF_6^- anion by comparison with alkali metal hexafluoro-niobates and -tantalates[12], has been used to suggest that their solid state structures are $[MF_4L_4^+]$ $[MF_6^-]$[3, 5, 6]. Such assignments must be ambiguous as they ignore the effect of different lattice types on the observed spectra. The space group of MF_5py_2 (M = Nb or Ta) is $P_1{}^2$ (No. 4) or $P_{1/m}^{2}$ (No. 11)*, and an MF_6^- anion, if present, would have C_i, C_2, or C_1 site symmetry. Under these conditions some components of all six O_h modes are both IR and Raman active, and splitting of formally degenerate modes would be expected. There is no unambiguous evidence for the presence of NbF_6^- anions in the spectrum of NbF_5py_2 (Table 3), and we suggest that molecular, 7-coordinate structures are equally likely for the 1:2 complexes in the solid state.

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