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^{19}F NMR spectroscopy as useful tool for determining the structure in solution of coordination compounds of MF_5 (M = Nb, Ta)

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ABSTRACT

The salts $[S(NMe_2)_3][MF_6]$ (M = Nb, **2a**; M = Ta, **2b**) and $[S(NMe_2)_3][M_2F_{11}]$ (M = Nb, **2c**; M = Ta, **2d**) have been prepared by reacting MF_5 (M = Nb, **1a**; M = Ta, **1b**) with $[S(NMe_2)_3][SiMe_3F_2]$ (TASF reagent) in the appropriate molar ratio. The solid state structure of **2b** has been ascertained by X-ray diffraction. The 1:1 molar ratio reactions of **1a** with a variety of organic compounds (L) give the neutral adducts NbF_5L [L = Me_2CO, **3a**; L = MeCHO, **3b**; L = Ph_2CO, **3c**; L = tetrahydrofuran (thf), **3d**; L = MeOH, **3e**; L = EtOH, **3f**; L = $HOCH_2CH_2OMe$, **3g**; L = Ph_3PO, **3h**; L = NCMe, **3i**] in good yields. The complexes MF_5L [M = Nb, L = $HCONMe_2$, **3j**; M = Nb, L = $(NMe_2)_2CO$, **3k**; M = Ta, L = $(NMe_2)_2CO$, **3l**; M = Nb, L = OC(Me)CH=CMe$_2$, **3m**] have been detected in solution in admixture with other unidentified products, upon 2:1 molar reaction of **1** with the appropriate reagent L. The ionic complexes $[NbF_4(tht)_2][NbF_6]$, **4a**, and $[NbF_4(tht)_2][Nb_2F_{11}]$, **4b**, have been obtained by combination of tetrahydrothiophene (tht) and **1a**, in 1:1 and 2:3 molar ratios, respectively. The treatment of **1** with a two-fold excess of L leads to the species $[MF_4L_4][MF_6]$ [M = Nb, L = $HCONMe_2$, **5a**; M = Ta, L = $HCONMe_2$, **5b**; M = Nb, L = thf, **5c**; M = Ta, L = thf, **5d**; M = Nb, L = OEt_2, **5e**]. The new complexes have been fully characterised by NMR spectroscopy. Moreover, the revised ^{19}F NMR features of the known compounds MF_5L [M = Ta, L = Me_2CO, **3n**; M = Ta, L = Ph_2CO, **3o**; M = Ta, L = MePhCO, **3p**; M = Ta, L = thf, **3q**; M = Nb, L = CH_3CO_2H, **3r**; M = Nb, L = CH_2ClCO_2H, **3s**; M = Ta, L = CH_2ClCO_2H, **3t**], TaF_4(acac), TaF_4(Me-acac) and $[TaF(Me\text{-}acac)_3][TaF_6]$ (Me-acac = methylacetylacetonato anion) are reported.

1. Introduction

The coordination chemistry of niobium and tantalum pentahalides MX_5 (M = Nb, Ta; X = halogen) [1] with oxygen donor ligands was scarcely investigated in the past [2], and recent work by ourselves has attempted a rationalization in this field [3]. Despite the scarce information available for that chemistry, the use of MCl_5 in catalysis has been progressively grown in the last decade [4]; these highly oxophilic compounds often provide noticeable results in metal-directed organic reactions, moreover they can exhibit unusual behaviour compared to different early transition metal halides in high oxidation state [5].

As far as niobium and tantalum pentafluorides MF_5 (M = Nb, **1a**; M = Ta, **1b**) are concerned, a restricted number of coordination adducts have been described [3a–d,6] and no X-ray structures have been reported hitherto. On the other hand, the fluoro-containing complexes **1** have found application as promoters of a variety of processes [7], including fluorination [8] and alkylation [9] reactions. Recent results have indicated that **1** may be used as efficient catalysts for ring opening polymerisations [10].

A close examination of the literature has shown that most of the reported niobium and tantalum fluoride containing species, including adducts of MF_5 and of the $[MF_6]^-$ anion, have not been isolated and their structure has been proposed on the basis of solution NMR spectroscopy (^{93}Nb, ^{19}F) [6a–c,e–i,11]. Unfortunately, the NMR data available in the literature often refer to solvents which react with the metal fluoride (ether, alcohols, nitriles, trifluoroacetic acid, fluorine, hydrogen fluoride), therefore an homogeneous, overall view of the situation is not possible at present.

In order to put some more light in the chemistry of MF_5 (M = Nb, Ta) and with the aim to give a contribution to the development of the use of these interesting compounds in metal-mediated syntheses, we decided to perform a systematic study on the coordination chemistry of **1** with a series of organic substrates, including oxygen-, nitrogen- and sulphur donor ligands. We have found that ^{19}F NMR spectra, recorded at the same temperature and

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in the same solvent, represent a useful tool for detecting the structure in solution of the MF_5 derivatives (M = Nb, Ta). In addition, this characterisation can be coherently supported by electrical conductivity data [12]. The present paper contains the results of our systematic study, which has also allowed to revise some attributions of ^{19}F NMR resonances reported in former reports by ourselves [3a–d].

2. Results and discussion

Our investigation started with the preparation and the full characterization of well defined MF_5 (M = Nb, Ta) derivatives to be used as "standard" for the subsequent analyses. Colourless solutions containing $SiMe_3F$ and $[S(NMe_2)_3][MF_6]$ (M = Nb, **2a**; M = Ta, **2b**), Eq. (1), were obtained by treatment of MF_5 with one equivalent of $[S(NMe_2)_3][SiMe_3F_2]$ (TASF reagent) in CH_2Cl_2. Crystalline compounds could be isolated by layering the solutions with heptane. The compounds **2a**,**b**, which display a very good solubility in chloroform, have been characterised by ^1H, ^{13}C and ^{19}F NMR spectroscopies, and by X-ray crystallography in the case of M = Ta.

$$[S(NMe_2)_3][SiMe_3F_2] + MF_5 \rightarrow \underset{\mathbf{2a,b}}{[S(NMe_2)_3][MF_6]} + SiMe_3F \tag{1}$$

Similarly, the derivatives $[S(NMe_2)_3][M_2F_{11}]$ (M = Nb, **2c**; M = Ta, **2d**) [11d] were prepared in solution by reacting pure **2a**,**b** with one equivalent of MF_5, Eq. (2), and characterised by ^{19}F NMR spectroscopy. Alternatively, orange $CDCl_3$ solutions of **2c**,**d** are obtainable by direct treatment of TASF with an excess of MF_5 (two equivalents or more).

$$\underset{\mathbf{2a,b}}{[S(NMe_2)_3][MF_6]} + MF_5 \rightarrow \underset{\mathbf{2c,d}}{[S(NMe_2)_3][M_2F_{11}]} \tag{2}$$

The crystal structure of **2b** (Fig. 1 and Table 1) consists in an ionic packing of $[TaF_6]^-$ anions and $[S(NMe_2)_3]^+$ cations. Some short inter-molecular contacts (in the range 2.50–2.66 Å) are present between the fluorine atoms of the anions and the H-methyl protons of the cations (sum of the Van der Waals radii 2.80 Å [13]). The $[TaF_6]^-$ anion displays the expected [14] octahedral geometry with the Ta–F bond distances comprised in a narrow range [1.878(5)–1.904(4) Å; average 1.888(10) Å]. The structure of the $[S(NMe_2)_3]^+$ cation is in keeping with previous structural determinations reported in the literature [15].

The ^1H and ^{13}C NMR spectra of **2a**,**b** (in $CDCl_3$ solution) display the resonance due to three equivalent methyl groups within the cation [*e.g.* in the case of **2a**: $\delta(^1H) = 2.96$ ppm, $\delta(^{13}C) = 38.4$ ppm]. An unique ^{19}F NMR signal accounts for six equivalent fluorines belonging to the anion. More precisely, a singlet at 39.1 ppm is observed in the ^{19}F NMR spectrum of **2b** (in $CDCl_3$), while the ^{19}F NMR resonance related to **2a** appears as a decet centered at 103.5 ppm [6a,11c,d], see Fig. 2, due to coupling of the fluorines with the niobium nucleus, characterized by $I = 9/2$. The absence of a well resolved octet for the $[TaF_6]^-$ anion (the tantalum nucleus has $I = 7/2$) is probably due to fast quadrupole relaxation of tantalum causing line broadening, thus affording a single broad peak even at low temperature [6g]. The $[M_2F_{11}]^-$ fluorines in the compounds **2c**,**d** appear equivalent at room temperature (in $CDCl_3$ solution), as result of fast exchange process. The related ^{19}F NMR resonances have been seen at 135.2 ($[Nb_2F_{11}]^-$) and 77.6 ($[Ta_2F_{11}]^-$) ppm, respectively. Conversely, low temperature NMR experiments (in $CDCl_3$ or CD_2Cl_2) have allowed to distinguish three distinct resonances [*e.g.* for **2d**: $\delta = 115.8$ (2 F, F1), 70.8 (8 F, F2), −73.9 (1 F, F3) ppm, see Fig. 3], in accord with what reported previously for the salts $[NBu_4][M_2F_{11}]$ (M = Nb, Ta) [11d].

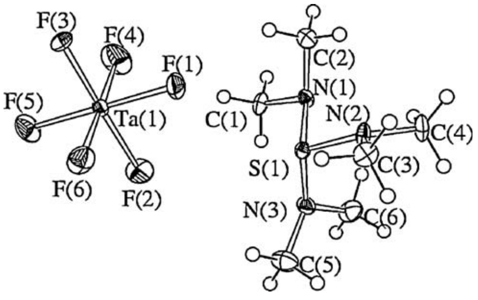

Fig. 1. View of the structure of $[S(NMe_2)_3][TaF_6]$, **2b**. Displacement ellipsoids are at 50% probability level.

Table 1
Selected bond distances (Å) and angles (°) of $[S(NMe_2)_3][TaF_6]$, **2b**.

F(1)–Ta(1)	1.888(4)	F(2)–Ta(1)	1.904(4)
F(3)–Ta(1)	1.895(4)	F(4)–Ta(1)	1.878(5)
F(5)–Ta(1)	1.884(4)	F(6)–Ta(1)	1.882(4)
N(1)–S(1)	1.693(4)	N(2)–S(1)	1.614(6)
N(3)–S(1)	1.626(6)		
C(1)–N(1)	1.484(9)	C(2)–N(1)	1.493(10)
C(3)–N(2)	1.464(8)	C(4)–N(2)	1.472(8)
C(5)–N(3)	1.462(9)	C(6)–N(3)	1.468(9)
N(2)–S(1)–N(3)	116.5(3)	N(2)–S(1)–N(1)	100.2(3)
N(3)–S(1)–N(1)	98.3(3)	C(1)–N(1)–C(2)	110.9(4)
C(1)–N(1)–S(1)	112.5(4)	C(2)–N(1)–S(1)	110.7(5)
C(3)–N(2)–C(4)	116.3(5)	C(3)–N(2)–S(1)	116.2(5)
C(4)–N(2)–S(1)	122.6(4)	C(5)–N(3)–C(6)	114.6(5)
C(5)–N(3)–S(1)	114.2(5)	C(6)–N(3)–S(1)	122.9(5)

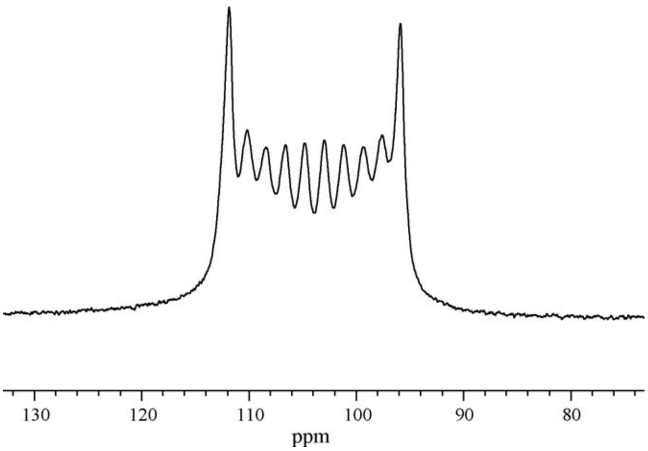

Fig. 2. The ^{19}F NMR spectrum of $[S(NMe_2)_3][NbF_6]$ (298 K, $CDCl_3$, $CFCl_3$ as external standard).

The reactions of **1** with equimolar amounts of a variety of organic compounds L, mainly oxygen donors, result in high yield formation of the neutral octahedral adducts $MF_5(L)$, **3a**–**i**,**n**–**t**, see Scheme 1. The analogous species **3j**–**m** could not be obtained cleanly, however they have been recognised in solution by NMR, upon reaction of **1** with L in 2:1 molar ratio.

Some of the reactions leading to the compounds **3** have been already described by ourselves [3a,c,d] or by other groups [6c,d].

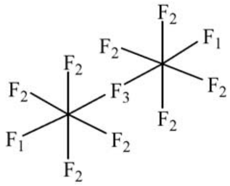

Fig. 3. Schematic drawing of the $[M_2F_{11}]^-$ (M = Nb, **2c**; M = Ta, **2d**) anion with fluorine numbering scheme.