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The Chemistry of Niobium and Tantalum Halides, MX_5, with Haloacetic Acids and their Related Anhydrides. Anhydride C–H Bond Activation Promoted by MF_5

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Niobium and Tantalum pentahalides, MX_5 (**1**), react with acetic acid and halo-substituted acetic acids, in 1:1 ratio, to give the dinuclear complexes $[MX_4(\mu\text{-OOCMe})]_2$ [M = Nb, X = Cl, **2a**; M = Ta, X = Cl, **2b**, Br, **2c**] and $[MCl_4(\mu\text{-OOCR})]_2$ [M = Nb, R = CH_2Cl, **4a**, $CHCl_2$, **4c**, CCl_3, **4e**, CF_3, **4g**, $CHBr_2$, **4i**, CH_2I, **4j**; M = Ta, R = CH_2Cl, **4b**, $CHCl_2$, **4d**, CCl_3, **4f**, CF_3, **4h**]. The solid state structures of **2b** and **4e** have been ascertained by X ray diffraction studies. The reactions of **1** with acetic anhydride and halo-substituted acetic anhydrides result in C-O bond activation and afford **2** and **4** respectively, with concomitant formation of acetyl halides. Moreover, the complexes $MCl_5[OC(Cl)Me]$ [M = Nb, **3a**; M = Ta, **3b**] have been detected in significant amounts within the mixtures of the reactions of MCl_5 with acetic anhydride. TaI_5 is unreactive, at room temperature, towards both CH_3COOH and $(CH_3CO)_2O$. MF_5 react with RCOOH (R = Me, CH_2Cl) in 1:1 molar ratio, to afford the ionic compounds $[MF_4(RCOOH)_2][MF_6]$, **5a-d**, in high yields. The additions of $(RCO)_2O$ (R = Me, CH_2Cl) to MF_5 give **5**, suggesting that anhydride C–H and C–O bonds activation is operative during the course of these reactions.

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Introduction

Although the coordination chemistry of Group 5 metal pentahalides [1] with oxygen donor ligands has been scarcely developed, the reactivity of $NbCl_5$ and $TaCl_5$ with acetic acid was first described eight decades ago.[2] Afterwards, adducts of formula $MCl_4(OOCR)$ (M = Nb, Ta, R = CH_3, CF_3, CCl_3, CH_2Br, $CHBr_2$, CBr_3), [3] beside a variety of oxo-chloride species of general formula $MOCl(OOCR)_2$,[3a,b,c] $MOCl_2(OOCR)$,[3a] $MO_2(OOCR)$,[3c] resulted from the reactions of MCl_5 with RCOOH or $(RCO)_2O$. However no unambiguous characterization was presented.

The chemistry of MCl_5 with aryl carboxylic acids has been better defined, and the dinuclear, carboxylato-bridged species $[MCl_4(OOCAr)]_2$ (M = Nb, Ta, Ar = aryl) have been reported.[4]

Interestingly, the dinuclear $Nb_2Cl_6(\mu\text{-O})(\mu\text{-OOCAr})_2$ [5] and the tetranuclear $Ta_4Cl_8(\mu\text{-O})_4(\mu\text{-OOCC}_6H_4Me\text{-}p)_4$ [6] μ-oxo species were isolated upon reacting MCl_5 with ArCOOH at high temperatures. These μ-oxo species were believed to be the result of *O*-abstraction by the metal from the carboxylate unit, activated at high temperature.

Recently, we have been involved in studying the chemistry of the coordination of *O*-donors to Group 5 metal pentahalides MX_5, **1**, (M = Nb, Ta, X = F, Cl, Br, I).[7]

According to these studies, the nature of the products depends basically on three factors: i) the *O*-donor reactant; ii) the metal/reactant ratio employed; iii) the halide. The influence of the halide on the outcome of the reactions of **1** with *O*-donors has been correlated to the metal-halide bond energy; markedly different chemical behaviours have been observed for X = Cl, Br, I and X = F. By contrast, the identity of the metal (Nb or Ta) has shown not to play a determinant role.[7] In consideration of the fact that the chemistry of MX_5 with carboxylate acids has been limited to the chlorides, and in order to put some more light into this topic, we decided to investigate the reactivity of **1** with haloacetic acids, and to extend the study to haloacetic anhydrides. The results of these studies will be presented and discussed herein.

Results and Discussion

1. Reactivity of MX_5 (M = Nb, Ta, X = Cl, Br, I) with acetic acid and acetic anhydride.

The compounds MX_5, **1**, in CH_2Cl_2 suspensions, react with acetic acid, in almost 1:1 molar ratio, to afford the dinuclear adducts $[MX_4(\mu\text{-OOCMe})]_2$ [M = Nb, X = Cl, **2a**; M = Ta, X = Cl, **2b**; M = Ta, X = Br, **2c**], in 75 ÷ 80 % yield, equation 1. No reaction between MeCOOH and TaI_5, suspended in CH_2Cl_2, occurs: as a matter of fact, the ^1H NMR of the mixture shows only the absorptions of uncoordinated acetic acid even after prolonged contact times.

$$2\,MX_5 + 2\,MeCOOH \rightarrow \underset{\textbf{2a-c}}{[MX_4(\mu\text{-OOCMe})]_2} + 2\,HX \qquad (1)$$

The products, **2a-c**, have been purified by crystallization, and have been fully characterized by means of IR and NMR spectroscopies, and elemental analysis. Moreover, the molecular structure of **2b** has been ascertained by X ray diffraction (Figure 1 and Table 1).

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The molecular structure of **2b** resembles the ones previously reported for the carboxylate bridged $[TaCl_4(\mu\text{-}OOCPh)]_2$ and $[NbCl_4(\mu\text{-}OOCC_6F_5]_2$ dimers. [4]. In the crystal structure, **2b** possesses C_i symmetry and only half of the molecule is present in the asymmetric unit. The distorted octahedrally coordinated Ta(V) centres display a *cis* arrangement of the ligands and the Ta–Cl bond distances [range 2.2857(11)-2.3393(11) Å; average 2.303(2) Å] are comparable to those present in other carboxylate bridged Ta(V) complexes such as the dinuclear $[TaCl_4(\mu\text{-}OOCPh)]_2$ [range 2.282(4)-2.308(4) Å; average 2.296(10) Å] [4] and the tetranuclear $Ta_4Cl_8(\mu\text{-}O)_4(\mu\text{-}OOCC_6H_4Me\text{-}p)_4$ [range 2.263(7)-2.322(4) Å; average 2.292(8) Å] [6]. Conversely, the Ta–O interactions [2.104(3) and 2.008(3) Å] display some asymmetry, whereas they are almost identical in $[TaCl_4(\mu\text{-}OOCPh)]_2$ [2.001(8) and 2.006(9) Å]. The C(1)–O(1) [1.260(5) Å] and C(1)–O(2)#1 [1.282(5) Å] distances are in agreement with a delocalised π-interaction and C(1) displays an almost perfect sp^2 hybridisation [sum angles 360.0(7)°]. The interatomic metal–metal distance [d(Ta–Ta) = 4.913(8) Å] indicates that no direct interaction between the two tantalum atoms occurs.

Insert Figure 1 about here.

Figure 1. Molecular structure of $[TaCl_4(\mu\text{-}OOCMe)]_2$, **2b**. Thermal ellipsoids are drawn at 30% probability level. Only independent atoms are labelled.

Table 1. Selected bond distances (Å) and angles (deg) of $[TaCl_4(\mu\text{-}OOCMe)]_2$, **2b.**

Ta(1)–Cl(1)	2.3393(11)	Ta(1)–O(2)	2.008(3)
Ta(1)–Cl(2)	2.2857(11)	C(1)–O(1)	1.260(5)
Ta(1)–Cl(3)	2.2977(11)	C(1)–O(2)#1	1.282(5)
Ta(1)–Cl(4)	2.2908(11)	C(1)–C(2)	1.485(6)
Ta(1)–O(1)	2.104(3)		
O(2)–Ta(1)–O(1)	86.15(12)	Cl(2)–Ta(1)–Cl(3)	95.38(4)
O(2)–Ta(1)–Cl(2)	91.83(9)	Cl(4)–Ta(1)–Cl(3)	95.81(4)
O(1)–Ta(1)–Cl(2)	177.94(8)	O(2)-Ta(1)–Cl(1)	84.07(9)
O(2)–Ta(1)–Cl(4)	172.86(9)	O(1)–Ta(1)–Cl(1)	86.06(9)
O(1)–Ta(1)–Cl(4)	87.54(9)	Cl(2)–Ta(1)–Cl(1)	94.14(4)
Cl(2)–Ta(1)–Cl(4)	94.50(4)	Cl(4)–Ta(1)–Cl(1)	92.16(4)
O(2)–Ta(1)–Cl(3)	86.87(9)	Cl(3)–Ta(1)–Cl(1)	167.05(4)
O(1)–Ta(1)–Cl(3)	84.11(9)	O(1)–C(1)–O(2)#1	120.5(4)
C(1)–O(1)-Ta(1)	138.2(3)	O(1)–C(1)–C(2)	120.1(4)
C(1)#1–O(2)–Ta(1)	143.3(3)	O(2)#1–C(1)–C(2)	119.4(4)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1.

The spectroscopic data collected for **2a-c** are coherent with the X ray features of **2b**. The ^{1}H NMR spectra (in CD_2Cl_2 solutions) exhibit one singlet due to the methyl groups, occurring at *ca.* 2.7 ppm. The ^{13}C NMR resonances are seen at *ca.* 185 (*C*OO) and 24 (*C*H$_3$) ppm. Furthermore, the IR spectra (recorded in the solid state) display the absorptions typical of bridging carboxylate moieties,[8] *e.g.* for **2a** at 1545 [ν_{as}(COO)] and 1489 [ν_s(COO)] cm^{-1}.

Since the chemistry of **1** with carboxylic anhydrides has been explored in less detail than that with the corresponding acids, we decided to study the reactions of MX_5 with the stoichiometric amount of acetic anhydride. Particular care was taken in order to have an anhydrous reaction system, so to eliminate the presence of adventitious water and/or of acetic acid. The complete absence of acetic acid was verified before each reaction by ^{1}H NMR spectroscopy.

Thus, the reactions of **1** (M = Nb, X = Cl, M = Ta, X = Cl, Br) with a slight excess of $(MeCO)_2O$ resulted in the formation of the dimeric species **2a-c**, equation 2. Coherently to what reported above, when compound TaI_5, in $CDCl_3$, was mixed with one equivalent of $(MeCO)_2O$, the ^{1}H NMR spectrum of the solution exhibited the resonances due to the free anhydride only.

$$2\,MX_5 + 2(MeCO)_2O \rightarrow \underset{\textbf{2a-c}}{[MX_4(\mu\text{-}OOCMe)]_2} + 2MeC(O)X \qquad (2)$$

When the reaction of MX_5 with a slight excess of acetic anhydride was performed in a NMR tube, the ^{1}H-NMR spectrum of the solution showed resonances due to **2**, MeCOX (X = Cl, Br) and to an additional compound characterized by a single resonance at *ca.* 2.8 ppm ($CDCl_3$, X = Cl). Although μ-oxo derivatives of niobium(V) and tantalum(V) have been obtained by reacting MCl_5 with acetic anhydride [3a, c], our present result suggests that a different compound is formed in our system.

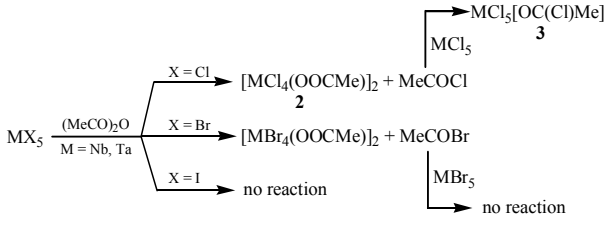
As a matter of fact, according to equation (2), see also [3c], the anhydride C–O bond activation produces MeCOX, a potentially good ligand for a strong Lewis acid such as MX_5 [7a, c]. In order to investigate the hypothesis that the compounds formed in admixture with **2** are adducts of acetyl chloride, MeC(O)Cl was added in 1:1 ratio to dichloromethane suspension of MCl_5: the soluble adducts $MCl_5[OC(Cl)Me]$ [M = Nb, **3a**; M = Ta, **3b**] formed rapidly, equation 3. It has to be noticed that $TaBr_5$ resulted unreactive towards MeC(O)Br.

$$MCl_5 + MeC(O)Cl \rightarrow \underset{\textbf{3a,b}}{MCl_5[OC(Cl)Me]} \qquad (3)$$

The complexes **3a-b**, which belong to the class of Lewis acid-base adducts of **1** with carbonyl compounds, have been isolated as microcrystalline solids upon removal of the volatile materials, and characterized by means of IR and NMR spectroscopies, and elemental analysis. The infrared carbonyl stretching vibration has been found at 1560 cm^{-1}, *i.e.* at significantly lower frequencies with respect to the uncoordinated acetyl chloride (1806 cm^{-1} [9]). The ^{1}H and ^{13}C NMR resonances appear downfield shifted with reference to free MeC(O)Cl: for instance, the ^{1}H resonance for the methyl group is seen at 2.81 ppm in **3a**, whereas it falls at 2.66 ppm in the case of uncoordinated MeC(O)Cl.[10]

At variance to what observed in the reactions of **1** with other C=O containing species [7a], the addition of a five-fold excess of acetyl chloride to $NbCl_5$ did not result in the formation of by-products. This evidence strongly suggests that only compounds **3** can result from combination of MCl_5 with *in situ* generated MC(O)Cl, in the reaction of MCl_5 with $(MeCO)_2O$.

On the basis of these results, it has to be concluded that the reactivity of MX_5 with acetic anhydride depends on the nature of X, and it can be summarized as in Scheme 1.



Scheme 1. The reactivity of MX_5 with acetic anhydride**.**

Indeed, when $NbCl_5$ was treated with $(MeCO)_2O$ in CD_2Cl_2 inside a NMR tube, some solid formed and the ^{1}H NMR spectrum of the solution revealed the presence [11] of **2a**, MeCOCl and **3a** in 1:3:7 molar ratio, which changed to 1:2:3 on increasing the $(MeCO)_2O$ /$NbCl_5$ molar ratio from 1 to 2.

The formation of **3a** was almost suppressed by using a $(MeCO)_2O$ /$NbCl_5$ molar ratio of 5. These evidences point out that acetyl chloride, formed as result of the anhydride fragmentation, competes with the uncoordinated anhydride to attack the unreacted inorganic substrate to give **3a**, causing a decreasing of the yield

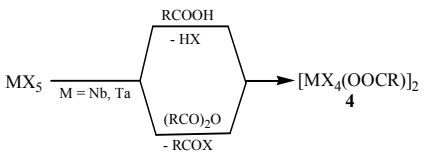
with which **2a** is obtained. The usage of an excess of anhydride limits the formation of **3a**. Under these conditions, we did not collect any evidence for the occurrence of *O*-abstraction reactions which appear instead to be the main process when the system is heated.[3a]

Considerations similar to what reported above are valid for the reaction of $TaCl_5$ with MeC(O)Cl (see Experimental for details). Furthermore, the reaction of $TaBr_5$ with acetic anhydride, followed by ^{1}H NMR spectroscopy, resulted in formation of **2c** and MeC(O)Br in 1:3 ratio: no traces of coordination adducts of MeC(O)Br with $TaBr_5$ were recognized, in accordance with the results of the studies on the reactivity of MX_5 with acetyl halides, discussed above.

2. Reactivity of MCl_5 (M = Nb, Ta) with halo-substituted acetic acids and acetic anhydrides.

The results presented in the previous section have pointed out that complexes **1** (M = Nb, Ta, X = Cl, Br) exhibit analogous reactivity towards acetic acid or acetic anhydride. Nevertheless, the dinuclear acetato-complexes are obtained in high yields by using acetic acid as reactant, the use of the anhydride leading to lower yields.

In order to see if this chemistry could be extended to other acids/anhydrides, we studied the reactions of MCl_5 (M = Nb, Ta) with halo-substituted acetic acids and with the corresponding anhydrides. The reactions with halo acetic acids led to the isolation and identification of the complexes $[MCl_4(\mu\text{-OOCR})]_2$ [M = Nb, R = CH_2Cl, **4a**; M = Ta, R = CH_2Cl, **4b**, M = Nb, R = $CHCl_2$, **4c**; M = Ta, R = $CHCl_2$, **4d**, M = Nb, R = CCl_3, **4e**; M = Ta, R = CCl_3, **4f**, M = Nb, R = CF_3, **4g**; M = Ta, R = CF_3, **4h**; M = Nb, R = $CHBr_2$, **4i**; M = Nb, R = CH_2I, **4j**] in good yields, Scheme 2. In agreement with what reported in section 1, most of compounds **4** could be prepared alternatively by reacting **1** with the appropriate anhydride (scheme 2). These latter reactions are accompanied by production of RC(O)X, which has been detected by ^{1}H NMR in the reaction medium in the majority of the cases (see Experimental).



Scheme 2. Preparation of halo-acetato derivatives of Nb(V) and Ta(V).

From the ^{1}H NMR spectra of the mixtures, it can be argued that $CH_2ClCOCl$ and $CHCl_2COCl$ give coordination adducts with unreacted **1**, in agreement with what discussed about MeCOCl and MCl_5 (see above).

Compounds **4** have been characterized by IR and NMR spectroscopies, and elemental analyses. Moreover, the X ray molecular structure of **4e** has been determined (Figure 2 and Table 2).

The molecular structure of **4e** is closely related to the one of **2b**, being the replacement of Ta(V) with Nb(V) and $-CH_3$ with $-CCl_3$ the major differences. Also in this case, each metal centre is coordinated to four chloride ligands and two bridging carboxylates with a relative *cis* geometry of the ligands and a distorted octahedral coordination. Despite the fact that the two halves of **4e** are crystallographically independent, their bonding parameters are almost identical (see Table 2) and perfectly comparable to the ones reported for the analogous Nb(V) dimer $[NbCl_4(\mu\text{-OOCC}_6F_5)]_2$. [4]. Finally, it is noteworthy that the dimeric nature of both **2b** and **4e** originates an octa-membered ring, which is puckered in **2b** [mean deviation from the Ta(1)O(2)C(1)#1O(1)#1Ta(1)#1O(2)#1O(1) least squares plane 0.1882 Å] but almost planar in **4e** [mean deviation from the Nb(1)O(1)C(1)O(2)Nb(2)O(3)C(3)O(4) least squares plane 0.0850 Å].

Insert Figure 2 about here.

Figure 2. Molecular structure of $[\{NbCl_4(\mu\text{-OOCCl}_3)\}_2]$, **4e**. Thermal ellipsoids are drawn at 30% probability level.

Table 2. Selected bond distances (Å) and angles (deg) of $[\{NbCl_4(\mu\text{-OOCCl}_3)\}_2]$, **4e.**

Nb(1)–Cl(1)	2.3005(7)	Nb(2)–Cl(5)	2.3023(8)
Nb(1)–Cl(2)	2.2931(7)	Nb(2)–Cl(6)	2.3006(8)
Nb(1)–Cl(3)	2.2574(5)	Nb(2)–Cl(7)	2.2600(6)
Nb(1)–Cl(4)	2.2550(6)	Nb(2)–Cl(8)	2.2626(5)
Nb(1)–O(1)	2.0828(17)	Nb(2)–O(2)	2.1534(17)
Nb(1)–O(4)	2.1676(16)	Nb(2)–O(3)	2.0635(18)
O(1)–C(1)	1.244(3)	O(3)–C(3)	1.236(3)
O(2)–C(1)	1.231(3)	O(4)–C(3)	1.238(3)
C(1)–C(2)	1.553(3)	C(3)–C(4)	1.550(3)
O(1)–Nb(1)–O(4)	84.72(6)	O(3)–Nb(2)–O(2)	84.89(7)
O(1)–Nb(1)–Cl(4)	170.39(5)	O(3)–Nb(2)–Cl(7)	170.37(5)
O(4)–Nb(1)–Cl(4)	85.66(5)	O(2)–Nb(2)–Cl(7)	85.48(5)
O(1)–Nb(1)–Cl(3)	93.49(5)	O(3)–Nb(2)–Cl(8)	93.65(5)
O(4)–Nb(1)–Cl(3)	178.10(5)	O(2)–Nb(2)–Cl(8)	178.41(5)
Cl(4)–Nb(1)–Cl(3)	96.12(2)	Cl(7)–Nb(2)–Cl(8)	95.98(2)
O(1)–Nb(1)–Cl(2)	83.40(6)	O(3)–Nb(2)–Cl(6)	83.54(7)
O(4)–Nb(1)–Cl(2)	84.36(5)	O(2)–Nb(2)–Cl(6)	84.34(6)
Cl(4)–Nb(1)–Cl(2)	95.46(2)	Cl(7)–Nb(2)–Cl(6)	95.09(2)
Cl(3)–Nb(1)–Cl(2)	96.09(2)	Cl(8)–Nb(2)–Cl(6)	96.14(2)
O(1)–Nb(1)–Cl(1)	83.51(6)	O(3)–Nb(2)–Cl(5)	83.85(7)
O(4)–Nb(1)–Cl(1)	83.43(5)	O(2)–Nb(2)–Cl(5)	84.16(6)
Cl(4)–Nb(1)–Cl(1)	95.60(2)	Cl(7)–Nb(2)–Cl(5)	95.59(3)
Cl(3)–Nb(1)–Cl(1)	95.74(2)	Cl(8)–Nb(2)–Cl(5)	95.06(3)
Cl(2)–Nb(1)–Cl(1)	162.84(3)	Cl(6)–Nb(2)–Cl(5)	163.62(3)
O(2)–C(1)–O(1)	125.7(2)	O(3)–C(3)–O(4)	125.9(2)
O(2)–C(1)–C(2)	117.49(19)	O(3)–C(3)–C(4)	116.10(19)
O(1)–C(1)–C(2)	116.77(19)	O(4)–C(3)–C(4)	117.96(19)

The IR spectra display the bands attributed to the symmetric and asymmetric vibrations of the [COO] group. These are found in the ranges 1386÷1515 cm^{-1} and 1522÷1635 cm^{-1}, respectively. In particular, the values available for **4g** are coherent with those reported for bridging trifluoroacetato complexes.[12] More in general, the fact that the difference ν_{as}-ν_s results smaller than 200 cm^{-1} in every cases indicates that the carboxylato units behave as bidentate ligands, rather than monodentate.[8]

Major ^{13}C NMR feature is given by the resonance due to the carboxylic carbon, which falls in the range 166.2(**4h**)-182.7(**4j**) ppm. The ^{13}C signal related to the $[CF_3]$ unit, in **4g-h**, appears as a quartet due to coupling with three adjacent fluorines (J = 286 Hz). In addition, the ^{19}F NMR spectra (CD_2Cl_2 solutions) carried out on **4g-h** exhibit the singlet attributed to six equivalent fluorines, at *ca.* –74 ppm.

3. Reactivity of MF_5 (M = Nb, Ta) with haloacetic acids and haloacetic anhydrides.

The pentafluorides MF_5 (M = Nb, Ta) react with RCOOH (R = Me, CH_2Cl), in 1:1 molar ratio, to give the ionic compounds $[MF_4(RCOOH)_2][MF_6]$ [M = Nb, R = Me, **5a**; M = Ta, R = Me, **5b**; M = Nb, R = CH_2Cl, **5c**; M = Ta, R = CH_2Cl, **5d**], equation 4.

$$2\ MF_5 + 2\ RCOOH \rightarrow \underset{\textbf{5a-d}}{[MF_4(RCOOH)_2][MF_6]} \qquad (4)$$

The products **5a-d** have been characterized by IR, ^{1}H, ^{13}C and ^{19}F NMR spectroscopies, and elemental analyses. The ^{1}H NMR spectra exhibit the resonance accounting for the R unit and a down-field resonance (11.61 ppm for **5c**) accounting for one oxygen-bound proton deshielded with respect to the uncoordinated acid.[10] In the ^{13}C NMR spectra, the carboxylic carbon is observed in the range 176.1(**5d**)-183.9(**5a**) ppm.[13] The ^{19}F NMR spectra are particularly diagnostic in determining the structure of compounds **5**, since they display a resonance occurring at typical negative δ values (*e.g.* –132.2 ppm for **5c**), accounting for the

$[MF_6]^-$ anion, together with the broad resonance characteristic of the $[MF_4]$ moiety.[14] The IR spectra (solid state) are characterized by a strong absorption in the range 1616 ÷ 1661 cm^{-1}, ascribable to the carboxylic C=O bond of the RCOOH ligands, rather than to carboxylato units. For instance, the C–O stretching vibration is observed at 1635 cm^{-1} in the IR spectrum of **5b**: this value is significantly closer to 1714 cm^{-1} (uncoordinated MeCOOH, [9]), rather than to the wavenumbers (1545 ÷ 1558 cm^{-1}) found for the bidentate carboxylate moiety within **2a-c**. These data are in agreement with those observed in other metal complexes containing carboxylic acids as ligands, such as $Ru_2(PhCOO)_6(PhCOOH)_2$, [15] $[TiCl_2(RCOO)(RCOOH)]_2O$, R = Et, [16] Bu^t.[17]

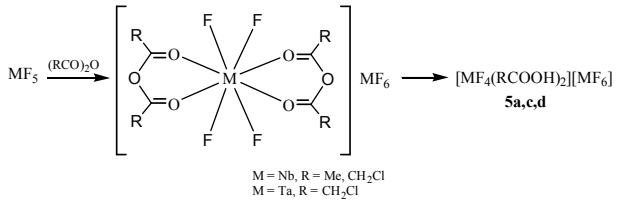
Unfortunately, due to the fact that we were not able to grow crystals suitable for X ray investigation, we cannot describe in more detail the structural features of the cation of **5**. The chemistry of MF_5 with acetic anhydride and chloroacetic anhydride was then investigated. We found that the reaction of NbF_5 with $(MeCO)_2O$, in 1:1 molar ratio, resulted in the clean formation of complex **5a**. On the other hand, TaF_5 gave a complicated and not well reproducible mixture of products on reaction with $(MeCO)_2O$, thus this was not investigated further. As far as chloroacetic anhydride is concerned, compounds **5c-d**, in admixture with minor by-products, could be isolated from the reactions with MF_5, equation 5.

$$MF_5 \xrightarrow[\substack{M = Nb,\ R = Me,\ CH_2Cl \\ M = Ta,\ R = CH_2Cl}]{(RCO)_2O} \underset{\textbf{5a,c,d}}{[MF_4(RCOOH)_2][MF_6]} \qquad (5)$$

The chemistry of MF_5 with anhydrides deserves some further comments, because a C–O bond activation and a protonation of an oxygen atom should occur in order to obtain the products of reaction (5). Three hypothesis may be formulated regarding the origin of the proton: it could descend i) from the anhydride itself, ii) from the solvent (CH_2Cl_2), or iii) from adventitious water.

In order to investigate the point, and paying particular attention to maintain strictly anhydrous conditions with anhydrides free from acid residues, we checked the reactions of NbF_5 with $(RCO)_2O$ (R = CH_3, CH_2Cl, one equivalent), in CD_2Cl_2, by NMR spectroscopy (see Experimental). The ^1H NMR spectra, taken 30 minutes after the mixing of the reactants, indicated clearly the formation of compounds **5a,c**. More specifically, the spectra exhibited the resonance of the O–*H* proton, which integrated for the correct ratio with respect to the resonance of the protons on the α-carbon atom, suggesting that the anhydride itself is the source of the proton.

The reaction of NbF_5 with $(CH_2ClCO)_2O$, being well slower than that with acetic anhydride, allowed an intermediate product to be detected and characterized. As a matter of fact, five minutes after the mixing of the reactants, the ^1H NMR spectrum indicated the complete disappearance of the free anhydride, and displayed only one resonance at 4.54 ppm. A quick ^{13}C NMR acquisition allowed to identify two peaks, at δ 167.4 (*C*O) and 48.7 (*C*H_2) ppm, respectively. Contextually, the ^{19}F NMR spectrum revealed the presence of the $[NbF_6]^-$ anion ($\delta = -133.0$ ppm, [14]). Twenty minutes later, the resonances attributed to **5c** clearly came out, together with signals ascribable to minor products. These results point to the conclusion that the reactions of MF_5 (M = Nb, Ta) with anhydrides $(RCO)_2O$ (R = CH_3, CH_2Cl) probably proceed *via* the formation of ionic intermediate species such as that reported in Scheme 3, in which two anhydrides coordinate the metal centre in a symmetric fashion:[3b] C–H and C–O bonds activation, and hydrogen migration to the oxygen atom, give the final, stable, products **5**. It has to be remarked that activation of C–H or C–O bonds occurs in the reactions of Group 5 metal halides with excess ketones (*e.g.* acetone, acetophenone), [7a] or ethers (the C–O bond activation represents a key step in the polymerization of tetrahydrofuran initiated by **1**). [7b,d]



Scheme 3. Mechanism proposed for the reactions of MF_5 with carboxylic anhydrides.

In view of the fact that the reaction of MF_5 with carboxylic ~~acid~~ anhydrides without hydrogen atoms on the α-carbon atom may potentially lead to the isolation of the intermediate represented in scheme 3, NbF_5 was treated with anhydrous $(CF_3CO)_2O$. Unfortunately, the reaction gave a mixture of inseparable and unidentifiable products. Notwithstanding, when the reaction was performed in a NMR tube (see Experimental), the ^{19}F NMR spectrum of the solution exhibited a peak awarded to the $[NbF_6]^-$ anion. Moreover, the ^1H NMR spectrum did not show any resonance, especially in the O-*H* region. Even though insufficient to establish the nature of the product, these observations are coherent with the structure placed into square brackets reported in scheme 3.

Conclusions

In this paper, we have presented the results concerning our research on the chemistry of niobium(V) and tantalum(V) pentahalides, MX_5, with haloacetic acids and haloacetic anhydrides.

According to our previous findings, the outcomes of the reactions do not generally depend on the metal but are strongly influenced by the nature of the halide: MCl_5 and MBr_5 show a similar behaviour in the reactions with acetic acids or anhydrides, whereas MF_5 show a fully different reactivity. To complete the picture, TaI_5 is inert towards both CH_3COOH and $(CH_3CO)_2O$.

The high stability of the $[MF_6]^-$ anion may be considered as the driving force of the reactions involving MF_5. As a consequence of such stability, HF is not released in the course of the reactions with acids, by contrast with what has been observed in the reactions of MX_5 (X = Cl, Br) with RCOOH.

More in detail, the reactions of MX_5 (X = Cl, Br) with haloacetic acids, which resemble those reported previously regarding the reactivity of $NbCl_5$ with aryl-carboxylic acids, proceed with releasing of HX and afford neutral dimeric complexes containing bridging coordinated acetates. On the other hand, MF_5 react with haloacetic acids with coordination of two intact acid molecules to the metal centre and contextual fluoride migration to give the $[MF_6]^-$ anion.

The reactions of MX_5 with anhydrides result in anhydride fragmentation and afford the same inorganic products obtained by the reactions with the corresponding acids, although in minor yields. With MX_5 (X = Cl, Br), anhydride C–O bond activation occurs, and the reactions proceed with releasing of acetyl halides, being the Lewis acid-base adducts of these latter with MX_5 the prevalent by-products. Beside, when MF_5 are involved, activation of both C–O and C–H bonds takes place within the anhydride, and proton migration afford final stable ionic species. These latter reactions can be accompanied by formation of complicated mixtures of minor products, which have not been identified.

All these investigations were conducted at room temperature, at which no evidences for the formation of *O*-abstraction products were found.

Experimental Section

All manipulations of air and/or moisture sensitive compounds were performed under an atmosphere of pre-purified argon using standard Schlenk techniques. The reaction vessels were oven dried

at 150 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. All the reagents, including MX_5 (M = Nb, Ta, X = Cl; M = Nb, Ta, X = F), were commercial products (Aldrich) of the highest purity available. $TaBr_5$ and TaI_5 [18] were prepared according to published procedures. Solid anhydrides and solid $CH_2ClCOOH$ were dried over P_4O_{10} and stored under argon atmosphere as received. Liquid acids and liquid anhydrides were distilled before use under argon atmosphere from P_4O_{10}. MeC(O)Cl and MeC(O)Br were distilled before use under argon atmosphere from molecular sieves. Liquid anhydrides were filtered through a short column of alumina immediately before use and their purity was verified by ^{1}H NMR. Solvents were distilled before use under argon atmosphere from appropriate drying agents: CH_2Cl_2, CD_2Cl_2, $CDCl_3$ from P_4O_{10}, pentane from $LiAlH_4$.

Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer equipped with a UATR sampling accessory (solid samples). NMR measurements were performed at 298 K on Varian Gemini 200BB spectrometer. The chemical shifts for ^{1}H-, ^{13}C-, and ^{19}F NMR spectra were referenced to TMS and to $CFCl_3$, respectively.

Carbon and hydrogen analyses were performed at the Dipartimento di Chimica Farmaceutica of the University of Pisa on a Carlo Erba mod. 1106 instrument, paying particular attention to the more sensitive compounds which were weighed and directly introduced into the analyzer. The halide content was determined by the Volhardt method [19] after exhaustive hydrolysis of the sample. The chlorocarboxylic acids did not give a precipitate of AgCl upon treatment with $AgNO_3$ under the conditions used for the hydrolysis of the sample. Metals were analyzed as M_2O_5 obtained by hydrolysis of the sample followed by calcination in a platinum crucible. The halide and the metal analyses were repeated twice in order to get reproducible results.

Preparation of $[MX_4(\mu\text{-OOCMe})]_2$ [M = Nb, X = Cl, 2a; M = Ta, X = Cl, 2b; Br, 2c].

General procedure: Acetic acid (0.031 mL, 0.54 mmol) was added to a suspension of MX_5 (0.500 mmol) in CH_2Cl_2 (25 mL), in a Schlenk tube. The mixture was stirred for 1 hour, and the final solution was layered with pentane (20 mL). A microcrystalline solid was formed after 24 hours at room temperature. In the same conditions, no reaction between TaI_5 and MeCOOH was observed. Crystals suitable for X ray analysis were collected from a solution of **2b** layered with pentane, at –20°C.

2a: $C_4H_6Cl_8Nb_2O_4$ (587.52), yellow: calcd. C 8.2, H 1.0, Nb 31.6, Cl 48.3; found C 8.4, H 1.0, Nb 31.0, Cl 47.9. Yield: 0.115 g, 78%. ^{1}H NMR (CD_2Cl_2) δ = 2.63 (s, 6 H, Me) ppm. ^{13}C NMR (CD_2Cl_2) δ = 185.4 (*C*O); 24.1 (Me) ppm. IR (solid state): ν = 2932w, 1545s [ν_{as}(COO)], 1489s [ν_s(COO)], 1387vs, 1340s, 1028w-m, 962w, 712vs cm^{-1}.

2b: $C_4H_6Cl_8O_4Ta_2$ (763.61), colourless: calcd. C 6.3, H 0.8, Ta 47.4, Cl 37.1; found C 6.4, H 0.7, Ta 47.2, Cl 36.7. Yield: 0.155 g, 81%. ^{1}H NMR (CD_2Cl_2) δ = 2.71 (s, 6 H, Me) ppm. ^{13}C NMR (CD_2Cl_2) δ = 185.9 (*C*O); 23.5 (Me) ppm. IR (solid state): ν = 2932wm, 2856wm, 1558s [ν_{as}(COO)], 1461s [ν_s(COO)], 1376m, 1344m, 1030m, 652m cm^{-1}.

2c: $C_4H_6Br_8O_4Ta_2$ (1119.22), orange: calcd. C 4.3, H 0.5, Ta 32.3, Br 57.1; found C 4.5, H 0.6, Ta 31.6, Br 56.1. Yield: 0.210 g, 75%. ^{1}H NMR (CD_2Cl_2) δ = 2.67 (s, 6 H, Me) ppm. ^{13}C NMR (CD_2Cl_2) δ = 186.3 (*C*O); 24.3 (Me) ppm. IR (solid state): ν = 2927w, 1545m-sh [ν_{as}(COO)], 1489s [ν_s(COO)], 1444vs, 1387vs, 1348m, 1262m, 1078w, 1029m, 939m, 804s, 680vs cm^{-1}.

Reactions of MX_5, 1 (M = Nb, X = Cl, M = Ta, X = Cl, Br, I), with $(MeCO)_2O$.

General procedure: Acetic anhydride (0.031 mL, 0.33 mmol) was added to a suspension of MX_5 (0.300 mmol) in CD_2Cl_2 (0.8 mL), inside a NMR tube, and the mixture was stirred for 30 minutes. Hence, a precipitate was present, and the ^{1}H NMR spectrum of the overlying solution appeared as follows: a) $NbCl_5$: **2a**, CH_3COCl and **3a** (vide infra) were detected in 1:3:7 ratios. b) $TaCl_5$: **2b**, CH_3COCl and **3b** in 1:3:3 ratios. c) $TaBr_5$: **2c** and CH_3COBr in 1:3 ratio. d) TaI_5: only resonances due to free anhydride were seen.

The reaction of acetic anhydride (0.50 mmol) with $NbCl_5$ (0.250 mmol), in CD_2Cl_2 (0.8 mL), gave a mixture consisting of **2a**, CH_3COCl and **3a** in 1:2:3 ratios.

Preparation of $[MCl_5\{OC(Cl)Me\}]$ [M = Nb, 3a; M = Ta, 3b].

General procedure: A suspension of MCl_5 (0.500 mmol) in CH_2Cl_2 (10 mL), in a Schlenk tube, was treated with MeC(O)Cl (0.043 mL, 0.60 mmol). The mixture was stirred for 30 minutes, during which progressive dissolution of the solid occurred. The final solution was dried in vacuo, and the resulting residue was washed with pentane (2 x 10 mL), affording microcrystalline **3**. The addition of a 5-fold excess of MeC(O)Cl to $NbCl_5$ (0.300 mmol), in $CDCl_3$ suspension, did result in the prevalent formation of **3a**, according to ^{1}H NMR spectroscopy. The addition of MeCOBr (0.035 ml, 0.47 mmol) to $TaBr_5$ (0.180 g, 0.310 mmol) in $CDCl_3$ (0.8 mL), inside a NMR tube, resulted in partial dissolution of the solid, but only uncoordinated MeCOBr was detected in solution by ^{1}H NMR.

3a: $C_2H_3Cl_6NbO$ (348.67), orange: calcd. C 6.9, H 0.9, Nb 26.6, Cl 61.0; found C 6.6, H 0.9, Nb 26.3, Cl 61.2. Yield: 0.148 g, 85%. ^{1}H NMR ($CDCl_3$) δ = 2.81 (s, 3 H, Me) ppm. ^{13}C NMR ($CDCl_3$) δ = 177.5 (CO); 34.2 (Me) ppm. IR (solid state): ν = 2957w, 2922w, 1560m (CO), 1479m, 1446s, 1393s, 1345ms, 1266m, 1154m, 1095m, 1028m, 880ms, 804vs, 778vs cm^{-1}.

3b: $C_2H_3Cl_6TaO$ (436.71), yellow: calcd. C 5.5, H 0.7, Ta 41.4, Cl 48.7; found C 5.4, H 0.8, Ta 40.9, Cl 48.3. Yield: 0.179 g, 82%. ^{1}H NMR ($CDCl_3$) δ = 2.79 (s, 3 H, Me) ppm. ^{13}C NMR ($CDCl_3$) δ = 175.6 (CO); 32.9 (Me) ppm. IR (solid state): ν = 2975w, 2922w, 1560s (CO), 1426m, 1391m, 1345m, 1265m, 1093m, 1031m, 940m, 807vs, 712s cm^{-1}.

Preparation of $[MCl_4(\mu\text{-OOCCH}_2\text{Cl})]_2$ [M = Nb, 4a; M = Ta, 4b]. General procedure: Chloroacetic acid (47 mg, 0.50 mmol) was added to MCl_5 (0.450 mmol), in CH_2Cl_2 (15 mL) suspension. The mixture was stirred for 1 hour and the final solution was layered with pentane (20 mL): precipitation of microcrystalline **4a-b** occurred after 12 hours at room temperature. Alternatively, the reactions of MCl_5 (0.20 mmol) with a slight excess of $(CH_2ClCO)_2O$, in CD_2Cl_2 (0.8 mL) inside NMR tubes, afforded solutions containing $CH_2ClCOCl$ and **4a-b** in *ca.* 3:1 ratio.

4a: $C_4H_4Cl_{10}Nb_2O_4$ (656.41), yellow: calcd. C 7.3, H 0.6, Nb 28.3, Cl 43.2; found C 7.1, H 0.7, Nb 27.9, Cl 42.9. Yield: 0.103 g, 70%. ^{1}H NMR (CD_2Cl_2) δ = 4.43 (s, 4 H, C*H*$_2$) ppm. ^{13}C NMR (CD_2Cl_2) δ = 179.2 (*C*O); 45.9 (*C*H$_2$) ppm. IR (solid state): ν = 2932w, 2886w, 1558m, 1522s [ν_{as}(COO)], 1386vs [ν_s(COO)], 1257s, 1152ms, 965m, 808m-s cm^{-1}.

4b: $C_4H_4Cl_{10}O_4Ta_2$ (832.49), light yellow: calcd. C 5.8, H 0.5, Ta 43.5, Cl 34.1; found C 5.6, H 0.5, Ta 43.1, Cl 34.0. Yield: 0.133 g, 71%. ^{1}H NMR (CD_2Cl_2) δ = 4.45 (s, 4 H, C*H*$_2$) ppm. ^{13}C NMR (CD_2Cl_2) δ = 180.4 (*C*O); 45.8 (*C*H$_2$) ppm. IR (solid state): ν = 2999w, 2958w, 1558s, 1532vs [ν_{as}(COO)], 1386vs [ν_s(COO)], 1259s, 1174m, 970wm, 920m, 811m-s, 656m cm^{-1}.

Preparation of $[MCl_4(\mu\text{-OOCCHCl}_2)]_2$ [M = Nb, 4c; M = Ta, 4d]. General procedure: These compounds were prepared by a procedure analogous to that described for **4a-b,** by reacting MCl_5 (0.400 mmol) with $CHCl_2COOH$ (0.036 mL, 0.44 mmol), for 2 hours. The reactions of MCl_5 (0.20 mmol) with a slight excess of $(CHCl_2CO)_2O$, in CD_2Cl_2 (0.8 mL) inside NMR tubes, afforded solutions containing $CHCl_2COCl$ and **4c-d**, in *ca.* 2 : 1 ratio.

4c: $C_4H_2Cl_{12}Nb_2O_4$ (725.30), light brown: calcd. C 6.6, H 0.3, Nb 25.6, Cl 39.1; found C 6.4, H 0.3, Nb 25.1, Cl 38.6. Yield: 0.109 g, 75%. ^{1}H NMR (CD_2Cl_2) δ = 6.30 (s, 2 H, C*H*) ppm. ^{13}C NMR (CD_2Cl_2) δ = 173.4 (*C*O); 63.9 (*C*H) ppm. IR (solid state): ν = 3003w, 2957w, 2924w, 1601vs [ν_{as}(COO)], 1408s [ν_s(COO)], 1266w, 1231vs, 1095m, 973w, 816vs, 783vs, 709vs cm^{-1}.

4d: $C_4H_2Cl_{12}O_4Ta_2$ (901.38), light yellow: calcd. C 5.3, H 0.2, Ta 40.2, Cl 31.5; found C 5.2, H 0.2, Ta 39.3, Cl 31.1. Yield: 0.128 g, 71%. ^{1}H NMR (CD_2Cl_2) δ = 6.35 (s, 2 H, C*H*) ppm. ^{13}C NMR (CD_2Cl_2) δ = 172.7 (*C*O); 64.5 (*C*H) ppm. IR (solid state): ν = 3006w, 2981w, 2969w, 1609vs [ν_{as}(COO)], 1450m-s [ν_s(COO)], 1422vs, 1264wm, 1236s, 1095w, 978w, 943w, 818s, 786m, 713s, 659ms cm^{-1}.

Preparation of [MCl_4(μ-OOCCCl_3)]$_2$ [M = Nb, 4e; M = Ta, 4f]. **General procedure:** These compounds were prepared by a procedure analogous to that described for **4a-b,** by reacting MCl_5 (0.420 mmol) with CCl_3COOH (0.048 mL, 0.48 mmol), for 3 hours. Crystals suitable for X ray analysis were collected by a CH_2Cl_2 solution of **4e**, layered with pentane, at –20°C.

4e: $C_4Cl_{14}Nb_2O_4$ (794.19), yellow: calcd. C 6.0, Nb 23.4, Cl 35.7; found C 6.3, Nb 23.2, Cl 35.9. Yield: 0.113 g, 68%. ^{13}C NMR (CD_2Cl_2) δ = 170.5 (*C*O); 90.0 (*C*Cl_3) ppm. IR (solid state): ν = 1621vs [ν_{as}(COO)], 1505m [ν_s(COO)], 1393s, 1362ms, 1262w, 978m, 855vs, 823vs, 726vs, 682vs cm^{-1}.

4f: $C_4Cl_{14}O_4Ta_2$ (970.27), colourless: calcd. C 5.0, Ta 37.3, Cl 29.3; found C 4.8, Ta 36.9, Cl 28.8. Yield: 0.134 g, 66%. ^{13}C NMR (CD_2Cl_2) δ = 170.2 (*C*O); 90.1 (*C*Cl_3) ppm. IR (solid state): ν = 2962w, 1627vs [ν_{as}(COO)], 1515m [ν_s(COO)], 1404s, 1365m, 1264w, 985m, 860s, 824s, 728s, 684vs cm^{-1}.

Preparation of [{MCl_4(μ-OOCCF_3)}$_2$] [M = Nb, 4g; M = Ta, 4h]. **General procedure:** These compounds were prepared by a procedure analogous to that described for **4a-b,** by reacting MCl_5 (0.500 mmol) with CF_3COOH (0.045 mL, 0.61 mmol). Alternatively, compounds **4g-h** were obtained in comparable yields by reacting MCl_5 (0.25 mmol) with one equivalent of $(CF_3CO)_2O$.

4g: $C_4Cl_8F_6Nb_2O_4$ (695.47), yellow: calcd. C 6.9, Nb 26.7, Cl 40.8; found C 6.7, Nb 26.0, Cl 39.2. Yield: 0.130 g, 75%. ^{13}C NMR (CD_2Cl_2) δ = 165.2 (m, *C*O); 114.3 (q, $^1J_{CF}$ = 286 Hz, *C*F_3) ppm. ^{19}F NMR (CD_2Cl_2) δ = –73.5 (s, 6 F, C*F*$_3$) ppm. IR (solid state): ν = 2978m, 2932w, 1760m, 1635m-s [ν_{as}(COO)], 1464m [ν_s(COO)], 1383s, 1259w-m, 1208m, 1163m-s, 1099vs, 1011s, 918m, 832vs, 804vs cm^{-1}.

4h: $C_4Cl_8F_6O_4Ta_2$ (871.55), colourless: calcd. C 5.5, Ta 41.5, Cl 32.5; found C 5.2, Ta 41.1, Cl 32.0. Yield: 0.146 g, 67%. ^{13}C NMR (CD_2Cl_2) δ = 166.2 (m, *C*O); 114.9 (q, $^1J_{CF}$ = 286 Hz, *C*F_3) ppm. ^{19}F NMR (CD_2Cl_2) δ = –73.9 (s, 6 F, C*F*$_3$) ppm.

Preparation of [{$NbCl_4$(μ-OOCCHBr_2)}$_2$], 4i, and of [{$NbCl_4$(OOCCH_2I)}$_2$], 4j. **General procedure:** These compounds were prepared by a procedure analogous to that described for **4a-b,** by reacting $NbCl_5$ (0.600 mmol) with a slight excess of $CHBr_2COOH$ or CH_2ICOOH, respectively.

4i: $C_4H_2Br_4Cl_8Nb_2O_4$ (903.11), yellow: calcd. C 5.3, H 0.2, Nb 20.6; found C 5.1, H 0.2, Nb 19.8. Yield: 0.209 g, 77%. ^{1}H NMR (CD_2Cl_2) δ = 6.19 (s, 2 H, C*H*) ppm. ^{13}C NMR (CD_2Cl_2) δ = 175.5 (*C*O); 34.7 (*C*H) ppm.

4j: $C_4H_4I_2Cl_8Nb_2O_4$ (839.32), yellow: calcd. C 5.7, H 0.5, Nb 22.1; found C 5.6, H 0.6, Nb 20.9. Yield: 0.176 g, 70%. ^{1}H NMR (CD_2Cl_2) δ = 4.19 (s, 4 H, C*H*$_2$) ppm. ^{13}C NMR (CD_2Cl_2) δ = 182.7 (*C*O); -3.9 (*C*H_2) ppm.

Preparation of [MF_4(RCOOH)$_2$][MF_6] [M = Nb, R= Me, 5a; M = Ta, R= Me, 5b; M = Nb, R = CH_2Cl, 5c; M = Ta, R = CH_2Cl, 5d]. **General procedure:** A suspension of MF_5 (0.400 mmol) in CH_2Cl_2 (15 mL) was treated with RCOOH (0.42 mmol; R = Me, CH_2Cl). The mixture was stirred for 30 minutes and the resulting solution was layered with pentane (20 mL). Compounds **5a-d** were obtained as microcrystalline solids after 12 hours.

5a: $C_4H_8F_{10}Nb_2O_4$ (495.90), orange: calcd. C 9.7, H 1.6, Nb 37.5; found C 9.9, H 1.5, Nb 37.0. Yield: 0.084 g, 85%. ^{1}H NMR (CD_2Cl_2) δ = 12.28 (s, 2 H, O*H*), 2.35 (s, 6 H, Me) ppm. ^{13}C NMR (CD_2Cl_2) δ = 183.9 (*C*O), 22.2 (Me) ppm. ^{19}F NMR (CD_2Cl_2) δ = 151.2 (Nb*F*$_4$), –132.3 (Nb*F*$_6$) ppm. IR (solid state): ν = 3186w-br (O–H), 2944m, 2795m, 2519w-m, 1616vs (C=O), 1555vs, 1407w, 1370w, 1247m, 1053w, 918m, 852ms cm^{-1}.

5b: $C_4H_8F_{10}O_4Ta_2$ (671.98), pale yellow: calcd. C 7.1, H 1.2, Ta 53.9; found C 7.0, H 1.3, Ta 53.5. Yield: 0.117 g, 87%. ^{1}H NMR (CD_2Cl_2) δ = 12.10 (s, 2 H, O*H*), 2.21 (s, 6 H, Me) ppm. ^{19}F NMR (CD_2Cl_2) δ = 81.2 (Ta*F*$_4$), –131.7 (Ta*F*$_6$) ppm. IR (solid state): ν = 3253br-m (O–H), 2942w, 2537w-m, 1635vs (C=O), 1397s, 1358m, 1230m, 1051m, 1012s, 883s, 829s cm^{-1}.

5c: $C_4H_6Cl_2F_{10}Nb_2O_4$ (564.79), orange: calcd. C 8.5, H 1.1, Nb 32.9; found C 8.3, H 1.1, Nb 32.0. Yield: 0.094 g, 83%. ^{1}H NMR (CD_2Cl_2) δ = 11.61 (s, 2 H, O*H*); 4.38 (s, 4 H, C*H*$_2$) ppm. ^{13}C NMR (CD_2Cl_2) δ = 176.8 (*C*O); 40.8 (*C*H_2) ppm. ^{19}F NMR (CD_2Cl_2) δ = 156.0 (Nb*F*$_4$); –132.3 (Nb*F*$_6$) ppm. IR (solid state): ν = 3228w-br (O-H), 2956w, 1661vs (C=O), 1551m, 1432m, 1395ms, 1275m, 1203br-m, 906vs, 797vs cm^{-1}.

5d: $C_4H_6Cl_2F_{10}O_4Ta_2$ (740.87), pale yellow: calcd. C 6.5, H 0.8, Ta 48.8; found C 6.4, H 1.0, Ta 48.6. Yield: 0.120 g, 81%. ^{1}H NMR (CD_2Cl_2) δ = 11.59 (s, 2 H, O*H*); 4.34 (s, 4 H, C*H*$_2$) ppm. ^{13}C NMR (CD_2Cl_2) δ = 176.1 (*C*O); 40.9 (*C*H_2) ppm. ^{19}F NMR (CD_2Cl_2) δ = 83.3 (Ta*F*$_4$); –132.4 (Ta*F*$_6$) ppm. IR (solid state): ν = 3225m-br (O–H), 3013w, 2958w, 1630vs (C=O), 1555m, 1450m, 1390m-s, 1270m, 1170m, 1123s, 903s, 850m-s, 804s, 712m-s cm^{-1}.

Reactions of MF_5 (M = Nb, Ta) with $(MeCO)_2O$ and $(CH_2ClCO)_2O$. Complex NbF_5 (0.350 mmol), in CH_2Cl_2 suspension (15 mL), was treated with $(MeCO)_2O$ (0.036 mL, 0.38 mmol). The mixture was stirred for 1 hour, then the solvent was removed under vacuum. Hence, the resulting residue was washed with pentane (2 x 10 mL), giving a dark yellow solid. An aliquot of this solid was analyzed by ^{1}H NMR spectroscopy (CD_2Cl_2 solution), which revealed the presence of a mixture of products, being **5a** the prevalent one. The reaction of TaF_5 with $(MeCO)_2O$, which was carried out three times in conditions analogous to that described for NbF_5, afforded complicated mixtures of products and did not appear reproducible.

The reactions of MF_5 (0.400 mmol; M = Nb, Ta) with $(CH_2ClCO)_2O$ (72 mg, 0.42 mmol) in CH_2Cl_2, yielded yellow solids upon removal of the solvent under vacuo. These solids were dissolved in CD_2Cl_2 and analyzed by ^{1}H NMR spectroscopy. The resonances related to **5c-d** were found, together with minor signals due to unidentified by-products. The formation of **5c-d** was confirmed by IR spectroscopy.

Reaction of NbF_5 with $(CH_2ClCO)_2O$ followed by NMR. Compound NbF_5 (120 mg, 0.639 mmol), CD_2Cl_2 (0.8 mL) and $(CH_2ClCO)_2O$ were introduced into a NMR tube in the order given, and the mixture was stirred manually for ca. one minute. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded after 5 minutes: ^{1}H NMR δ = 4.54 (s, C*H*$_2$) ppm; ^{13}C NMR δ = 167.4 (*C*O); 48.7 (*C*H_2) ppm; ^{19}F NMR δ = –133.0 (Nb*F*$_6$) ppm. After thirty minutes, the ^{1}H NMR spectrum of the mixture indicated complete disappearance of the resonance at 4.54 ppm, formation of **5c** together with some by-products.

Reaction of NbF_5 with $(CF_3CO)_2O$. Complex NbF_5 (180 mg, 0.958 mmol), in suspension of CH_2Cl_2 (15 mL), was treated with $(CF_3CO)_2$ (0.12 mL, 0.90 mmol). The mixture was stirred for 2 hours, then the solvent was removed in vacuo. The resulting residue was washed with pentane (15 mL), thus a pale yellow solid was obtained. ^{19}F NMR (CD_2Cl_2) δ = –133.1 (Nb*F*$_6$) ppm. ^{1}H NMR (CD_2Cl_2): no resonances in the O–*H* region.

X-ray Crystallographic Study. Crystal data and collection details for [$TaCl_4$(μ-OOCMe)]$_2$, **2b**, and [$NbCl_4$(μ-OOCCCl_3)]$_2$, **4e**, are reported in Table 3. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using *Mo-Kα* radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction

SADABS). [20] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2. [21] Hydrogen atoms bonded to C-atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. In the crystal structure of **2b**, the asymmetric unit contains only half of the molecule. The crystal of **4e** is racemically twinned with a refined Flack parameter of 0.23(3) [22], and it was, therefore, refined using the TWIN refinement routine of SHELXTL.

Table 3. Crystal data and structure refinement for $[TaCl_4(\mu\text{-}OOCMe)]_2$, **2b**, and $[NbCl_4(\mu\text{-}OOCCCl_3)]_2$, **4e**.

Complex	**2b**	**4e**
Formula	$C_4H_6Cl_8O_4Ta_2$	$C_4Cl_{14}Nb_2O_4$
F*w*	763.59	794.16
T, K	100(2)	100(2)
λ, Å	0.71073	0.71073
Crystal system	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$Pca2_1$
a, Å	6.7746(9)	12.0031(7)
b, Å	6.9224(9)	14.6579(8)
c, Å	9.7855(13)	11.9975(7)
α, °	99.843(2)	90
β, °	104.818(2)	90
γ, °	106.174(2)	90
Cell volume, Å^3	411.33(9)	2110.8(2)
Z	1	4
D_c, g cm^{-3}	3.083	2.499
μ, mm^{-1}	14.588	2.867
F(000)	344	1504
Crystal size, mm	0.20×0.18×0.12	0.19×0.17×0.15
θ limits, °	2.23 – 26.99	1.39 – 27.99
Reflections collected	4501	17476
Independent reflections	1785 (R_{int} = 0.0327)	4984 (R_{int} = 0.0159)
Data/restraints/parameters	1785 / 0 / 83	4984 / 1 / 218
Goodness on fit on F^2	1.135	1.114
R_1 [$I > 2\sigma(I)$]	0.0216	0.0176
wR_2 (all data)	0.0561	0.0437
Largest diff. peak and hole, e.Å^{-3}	1.677 / – 2.117	0.482 / – 0.818

Supporting Information (see footnote on the first page of this article): CCDC reference numbers 674014 {$[TaCl_4(\mu\text{-}OOCMe)]_2$, **2b**} and 674013 {$[NbCl_4(\mu\text{-}OOCCCl_3)]_2$, **4e**}, contain the supplementary crystallographic data for the X-ray studies. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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Figure 1

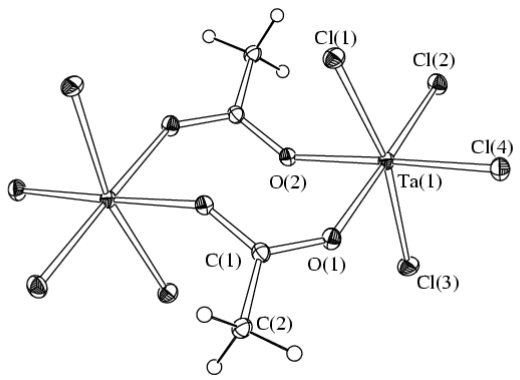
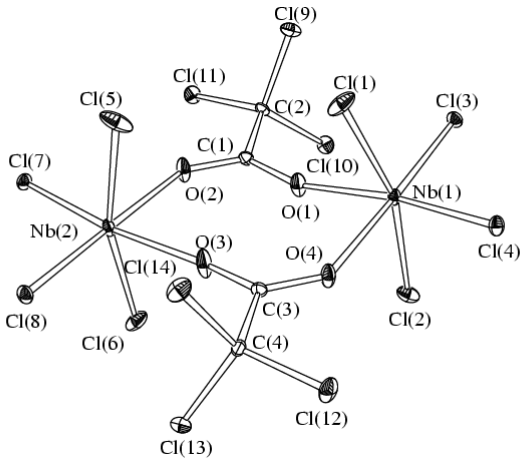


Figure 2

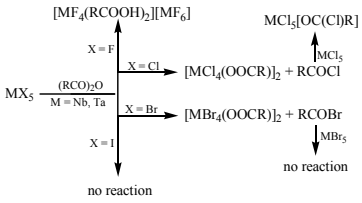


Entry for the Table of Contents

Layout 1:

((Key Topic))

The reactivity of MX_5, (M = Nb, Ta) with haloacetic acids or the corresponding anhydrides is strongly influenced by the nature of the halide: dinuclear carboxylates are obtained with chlorides and bromides, while the fluorides afford ionic compounds containing the $[MF_6]^-$ anion. The reaction of MF_5 with carboxylic anhydrides proceeds via C–O and C–H bonds activation.



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The Chemistry of Nb and Ta Halides MX_5 with HaloAcetic Acids and their Related Anhydrides. Anhydride C–H Bond Activation Promoted by MF_5

Keywords: Niobium, Tantalum, Pentahalides, Haloacetic acids, Anhydrides, Haloacetyl halides