Reactions of TaF_5 with Activated Arenes. Synthesis of $[4\text{-}(OH)\text{-}3\text{-}(OCH_3)C_6H_3CH(=O\text{-}H)][4\text{-}(OH)\text{-}3\text{-}(OCH_3)C_6H_3CHO][TaF_6]$, a Rare Example of Protonated Aldehyde

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Abstract

The rare example of protonated aldehyde salt [4-(OH)-3-(OCH_3)C_6H_3CH(=O–H)][4-(OH)-3-(OCH_3)C_6H_3CHO][TaF_6], **1**, was isolated in the solid state by the reaction of 4-hydroxy-3-methoxybenzaldehyde (vanillin) with TaF_5 in dichloromethane. The product **1** was characterized by X-ray diffraction and IR spectroscopy. The 1:1 reaction of TaF_5 with *N,N*-dimethylaniline in CH_2Cl_2 cleanly afforded [TaF_4($NMe_2C_6H_5$)$_2$][TaF_6], **2**, which was identified by NMR spectroscopy. Attempts of crystallization of **2** resulted in the isolation of the ammonium salt [$NHMe_2C_6H_5$][TaF_6], **3**.

Keywords: Tantalum pentafluoride, Crystal structure, protonated aldehydes, vanillin

1. Introduction

The isolation of uncommon cations has been possible in view of the availability of large, non coordinating and weakly-basic anions such as carboranes or fluorinated tetraphenylborates [1].

Niobium(V) and tantalum(V) haloanions (or mixed alkoxo-haloanions) have revealed to be effective for the stabilization of reactive cationic species such as *O*-protonated ketones [2], *O*-methylated ketones [3], diglyme [4], thioethers [5], indanyl- and anthryl cations [6].

The reactions of MF_5 with arenes bearing electron-donor substituents proceed through the initial coordination of the organic moiety to the metal fluoride [7], followed by activation. Thus arenium salts of formula [2,4-$(OMe)_2C_6H_5$][M_2F_{11}] (M = Nb, Ta) have been isolated in the solid state at room temperature from MF_5/1,3-dimethoxybenzene: they are robust species which resist thermal treatment in $CHCl_3$ [8]. Previously reported dialkoxybenzenium ions were detected at room temperature in concentrated H_2SO_4 [9] or, at low temperature, by using conventional superacidic systems (*e.g.* SbF_5/HF) [10].

Furthermore, deeply-coloured solutions of arene radical cation salts have been obtained by treatment of the appropriate monocyclic aromatic compound with MF_5 (M = Nb, Ta), according to Eq. (1) [11]. Radical salts lacking of electron-donor substituents have been produced in low yields by the same method.

$$3MF_5 + \text{Arene} \rightarrow [\text{Arene}][M_2F_{11}] + MF_4 \qquad (1)$$

Arene = alkyl-, alkoxy-, fluoro- and nitro-substituted benzenes

In general, adventitious hydrolysis [4, 5], activation of the organic substrate [2] and the solvent [8] are the possible proton sources for those reactions involving niobium and tantalum pentafluorides and leading to the protonation of the organic reactant.

Herein we report an extension of the investigation on the reactivity of TaF_5 [12,13] with activated arenes. To the purpose, a functionalized aromatic aldehyde, [4-(OH)-3-(OCH_3)C_6H_3CHO, vanillin], and an aromatic amine, N,N-dimethylaniline, have been considered. The reactions have afforded the rare example of crystallographically-characterized protonated aldehyde [4-(OH)-3-(OCH_3)$C_6H_3CH(=O–H)$][4-(OH)-3-(OCH_3)C_6H_3CHO][TaF_6], and the ionic derivative [$TaF_4(NMe_2C_6H_5)_2$][TaF_6], respectively.

2. Results and Discussion

The reaction of a dichloromethane suspension of TaF_5 with vanillin in molar ratio 1:1 afforded a complicated mixture of unidentified products, according to NMR spectroscopy. The crystalline salt [4-(OH)-3-(OCH_3)$C_6H_3CH(=O–H)$][4-(OH)-3-(OCH_3)C_6H_3CHO][TaF_6], **1**, was isolated in moderate amount by crystallization from the reaction mixture (Scheme 1); the use of higher vanillin/TaF_5 molar ratios resulted in yield decreasing.

Scheme 1 about here

Once isolated in the crystalline form, **1** is nearly insoluble in chlorinated solvents, while it undergoes quick degradation in more polar solvents (*e.g.* acetonitrile): these facts prevented a clear NMR characterization of **1**. The IR spectrum of **1** features a broad band centered at 3376 cm^{-1}, due to overlap of stretching vibrations of the covalent OH bond and of the $O\cdots H\text{-}O$ hydrogen bonding interaction. Vanillin, characterized by a different hydrogen bonding network, involving the OH group as proton-donor and the aldehydic oxygen as proton-acceptor [14], shows a broad absorption at lower wavenumbers (3212 cm^{-1}) [15]. The most salient feature of the IR spectrum of **1** is the absence of a strong absorption in the C=O carbonyl stretching region (a weak signal is present at 1622 cm^{-1}). A similar situation was reported for protonated 1-pyrene carboxaldehyde and 9-antraldehyde [16]. This fact may be the consequence of elongation of the C=O aldehydic bond [1.26(2) and 1.22(2) Å] with respect to free vanillin [1.202-1.206 Å], due to the formation of the hydrogen-bonded dimer (vide infra).

EPR analysis on the 1:1 reaction mixture TaF_5/vanillin was carried out after addition of acetonitrile, however no tantalum(IV) derivatives were detected [17]. This outcome suggests that radical species do not form in the course of the reaction [11], therefore the protonation of the organic compound cannot proceed *via* a redox process followed by H transfer (redox reactions were recognized for a series of TaF_5/alkoxyarene systems) [11c].

Instead, the formation of **1** is presumably the result of H^+ capture from the reaction medium, assisted by the high-stability of the $[TaF_6]^-$ anion, which can be generated upon asymmetric disruption of the tetranuclear frame of TaF_5 [13,18,19]. In principle, uncontrolled traces of water [5], the solvent and the reactant itself constitute the possible proton sources. The latter probably plays a significant role, in view of the favourable acidity (the pKa value of vanillin in water is 7.496) [20]. Attempts aimed to identify the side-products of the reaction did not provide conclusive information.

After several attempts, X-ray quality crystals of **1** were obtained by layering with heptane a dichloromethane solution of **1**, thus allowing a full characterization. An ORTEP representation of the content of the asymmetric unit of the unit cell of **1** is reported in Figure 1, whereas the main bonding parameters are summarized in Table 1. The salt is composed by an octahedral $[TaF_6]^-$ anion and a H-bonded $\{[4\text{-}(OH)\text{-}3\text{-}(OCH_3)C_6H_3CH(=O\text{–}H)][4\text{-}(OH)\text{-}3\text{-}(OCH_3)C_6H_3CHO]\}^+$ dimeric cation consisting of one protonated and one non protonated vanillin molecules. Protonation has occurred at the aldehyde O(6)-atom and the dimer is formed because of a strong H-bond involving O(6) and H(6) as donor and the free aldehydic O(3) atom of the non-protonated vanillin as acceptor. A representation of the cationic dimer is reported in Figure 2, whereas its hydrogen bond parameters are given in Table 2. The O(6)···O(3) distance [2.48(2) Å] is typical of a strong H-bond, as previously found in the very few other examples of protonated aldehydes reported in the literature [16]. As a consequence of the protonation of O(6) and formation of the strong O(6)–H(6)···O(3) hydrogen bond, the two C=O aldehyde units [C(8)–O(3) 1.26(2) Å; C(18)–O(6) 1.22(2) Å] are sensibly elongated compared to free vanillin [1.202-1.206 Å] [14]. In addition, the hydroxyl O(1)–H(1) group of the non-protonated vanillin is involved as donor in a weaker hydrogen bond towards the hydroxyl O(4) atom of a second protonated vanillin, resulting in an infinite chain of alternate protonated and non-protonated molecules. An intramolecular O(1)–H(1)···O(2) hydrogen bond is present as well as a O(4)–H(4)···F(5) contact, the latter involving the O(4)–H(4) hydroxyl group of the free vanillin as donor and the $[TaF_6]^-$ anion as acceptor (Table 2). The presence of several strong and weak O–H···O and O–H···F hydrogen bonds results in the ordered 3-D packing of the salt as represented in Figure S1 (Supporting Information). It must be noticed that, in crystalline vanillin, a hydrogen bond network is present, involving the hydroxyl group as donor and the aldehydic oxygen as acceptor [14] (Figure S2).

Figures 1and 2, Tables 1 and 2 about here

We extended the present study to the reactivity of tantalum pentafluoride with arene molecules containing a nitrogen-based substituent. The clearest result was obtained by the 1:1 reaction of TaF_5 with *N*,*N*-dimethyalaniline, which was carried out in dichloromethane. This reaction selectively afforded a green solution of the well-soluble salt $[TaF_4(NMe_2C_6H_5)_2][TaF_6]$, **2**. This compound has been characterized by NMR on a green CD_2Cl_2 reaction mixture. The *N*-bound methyls resonate as single peaks in both ^1H and ^{13}C NMR spectra (δ = 3.28 and 48.0 ppm, respectively). Such resonances are significantly low-field shifted compared to what is seen in uncoordinated *N,N*-dimethylaniline (δ = 2.89 and 40.50, respectively) [21], thus suggesting the engagement of the amino-group in coordination to the metal centre. The ^{19}F NMR spectrum consists of a resonance at 40.3 ppm, accounting for the $[TaF_6]^-$ anion [18a,19,22] and indicating the occurrence of asymmetric cleavage of the tetranuclear Ta_4F_{20} frame upon addition of the organic reactant [18a,19]. As often occurs, the resonance due to the $[TaF_4]^+$ moiety is not observed in the ^{19}F spectrum of compound **2** [22b].

All of the attempts to obtain X-ray quality crystals of **2** failed. Nonetheless one of these attempts led to the low-yield isolation of the ammonium salt $[NHMe_2C_6H_5][TaF_6]$, **3**. The ^1H-NMR of this latter clearly displays a broad resonance ascribable to the nitrogen-bonded proton, at δ = 9.03 ppm. The presence of the NH moiety has been confirmed by a medium absorption occurring at 3194 cm^{-1} in the solid state IR spectrum (N-H stretching vibration). The resonance at 40.0 ppm in the ^{19}F-spectrum is diagnostic for the presence of the $[TaF_6]^-$ anion.

The formation of **3** appears to be the consequence of H^+ capture from the reaction medium, presumably made possible by the presence of adventitious water, Scheme 2.

Scheme2 about here

3. Conclusions

In this paper, we have described the synthesis and the structural properties of a rare example of protonated-aldehyde salt, as obtained from the reaction of TaF_5 with vanillin. The product consists of an octahedral $[TaF_6]^-$ anion and a H-bonded $\{[4\text{-}(OH)\text{-}3\text{-}(OCH_3)C_6H_3CH(=O\text{–}H)][4\text{-}(OH)\text{-}3\text{-}(OCH_3)C_6H_3CHO)]\}^+$ dimeric cation, formally made of one vanillin molecule linked to one aldehyde-O-atom-protonated vanillin. The combination of the acidity of vanillin [20] with the high stability of the $[TaF_6]^-$ ion may be the driving force for the formation of such product.

On the other hand, the reaction of *N,N*-dimethylaniline with TaF_5 selectively produces the ionic derivative $[TaF_4(NMe_2C_6H_5)_2][TaF_6]$. The solid state isolation of the relevant ammonium salt has been presumably made possible by the action of adventitious water.

4. Experimental

4.1. General procedures

All manipulations of air and/or moisture sensitive compounds were performed under 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 nitrogen. TaF_5 was purchased from Apollo Sci. (99% purity), sublimed prior to use and stored in sealed glass tubes under argon atmosphere. The organic reactants were commercial products (Sigma-Aldrich) stored under argon atmosphere as received. Solvents (Sigma-Aldrich) were distilled before use from appropriate drying agents. Infrared spectra were recorded at 298 K on FT IR Spectrum One Perkin Elmer Spectrometer, equipped with UATR sampling accessory. NMR spectra were recorded at 293 K on Bruker Avance DRX400 instrument equipped with BBFO broadband probe. The chemical shifts for ^1H and ^{13}C spectra were referenced to the non-deuterated aliquot of the solvent, while the chemical shifts for ^{19}F spectra were referenced to $CFCl_3$. ^1H and ^{13}C NMR assignments were assisted by HSQC and HMBC experiments [23]. Carbon, hydrogen and nitrogen analyses were performed on Carlo Erba mod. 1106 instrument. The fluoride content was determined by fluoride ion selective electrode, after boiling the sample in alkaline solution. Tantalum was analyzed as Ta_2O_5 obtained by high temperature treatment of the solid sample with HNO_3 solution, followed by calcination in a platinum crucible.

4.2. Preparation of [4-(OH)-3-(OCH$_3$)C$_6$H$_3$CH(=O–H)][4-(OH)-3-(OCH$_3$)C$_6$H$_3$CHO] [TaF$_6$], **1.** TaF_5 (0.129 g, 0.467 mmol) was allowed to react with vanillin (0.072 g, 0.470 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 15 h at room temperature, and the colour progressively changed from colourless to green. The final mixture was filtered in order to remove some dark-green precipitate; the filtrated green solution was layered with heptane and stored at room temperature for 72 h. Hence a crop of green crystals of **1** were collected. Yield: 0.101 g, 36% (based on Ta). Anal. Calcd for $C_{16}H_{17}F_6O_6Ta$: C, 32.01; H, 2.85; F, 18.99; Ta, 30.14. Found: C, 31.75; H, 2.70; F, 18.12; Ta, 28.95. IR (solid state): ν = 3376m-br (O–H), 2961w, 2921w, 1574vs-br (C=O), 1511vs-sh, 1506vs, 1467m-s, 1434m, 1410w, 1301s, 1272s, 1169s, 1124m, 1024m, 866w-m, 824w, 783w, 734w-m cm^{-1}.

The reaction of TaF_5 (0.30 mmol) with vanillin (0.30 mmol), carried out in CD_2Cl_2 (1.0 mL), afforded a green solution which was analyzed by NMR. A mixture of unidentified products was detected.

4.3. Isolation of [NHMe$_2$C$_6$H$_5$][TaF$_6$], ***3****, and NMR characterization of [TaF$_4$(NMe$_2$C$_6$H$_5$)$_2$][TaF$_6$],* ***2****.* A suspension of TaF_5 (0.205 g, 0.743 mmol) in dichloromethane (15 mL) was treated with *N,N*-dimethylaniline (0.095 mL, 0.750 mmol), and the resulting mixture was stirred for 18 h at room temperature. The final product **3** was obtained as colourless crystalline material upon crystallization from the green reaction solution layered with heptane, at –30 °C. Yield: 0.041 g, 13% (based on Ta). Anal. Calcd for $C_8H_{12}F_6NTa$: C, 23.03; H, 2.90; N, 3.36; F, 27.33; Ta, 43.38. Found: C, 23.12; H, 2.74; N, 3.28; F, 26.86; Ta, 43.20. IR (solid state): ν

= 3194m (N–H), 3068w, 2977w, 2891w, 1600w–m, 1489s, 1468m–s, 1416m, 1361w–m, 1131s, 1082m, 1048m, 1025m, 985s, 898vs, 771s, 761vs, 696vs cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 9.03 (br, 1 H, NH), 7.67 - 7.55 (m, 5 H, Ph), 3.43, 3.41 (s, 6 H, Me) ppm. ^{13}C NMR (CD_2Cl_2): δ = 141.6 (*ipso*-Ph), 131.2, 131.1, 119.9 (Ph), 48.2 (Me) ppm. ^{19}F NMR (CD_2Cl_2): δ = 40.0 ($[TaF_6]^-$) ppm.

The addition of *N,N*-dimethylaniline (0.080 mL, 0.632 mmol) to TaF_5 (0.150 g, 0.634 mmol) in CD_2Cl_2 (0.60 mL) quickly afforded a green solution which was analyzed by NMR spectroscopy, thus allowing the characterization of **2**. ^{1}H NMR (CD_2Cl_2): δ = 7.50, 7.42, 7.31 (m, 5 H, Ph), 3.28 (s, 6 H, Me) ppm. ^{13}C NMR (CD_2Cl_2): δ = 148.1 (*ipso*-Ph), 129.5, 125.8, 119.1 (Ph), 48.0 (Me) ppm. ^{19}F NMR (CD_2Cl_2): δ = 40.3 ($[TaF_6]^-$) ppm.

4.4. X-ray Crystallographic Study.

Crystal data and collection details for **1** are listed in Table 3. The diffraction experiments were carried out on Bruker APEX II diffractometer equipped with CCD detector and using Mo-Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS) [24]. The structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 [24].All non-hydrogen atoms were refined with anisotropic displacement parameters. H-atoms were placed in calculated positions and treated isotropically using the 1.2 fold U_{iso} value of the parent atom except methyl protons, which were assigned the 1.5 fold U_{iso} value of the parent C-atom. The O-bonded H-atoms were initially located in the Fourier map but, then, they were refined with a riding model. Similar *U* restraints (*s.u.* 0.01) were applied to the C, O and F atoms. The F-atoms were restrained to an isotropic like behaviour (ISOR line in SHELXL; *s.u.* 0.01).

Tables 3 about here

Supplementary Data

Figure S1 reports a view of the crystal packing of **1** along the crystallographic (A) a-axis, (B) b-axis and (C) c-axis. Figure S2 represents the hydrogen-bond linking in solid vanillin. CCDC reference number 949676 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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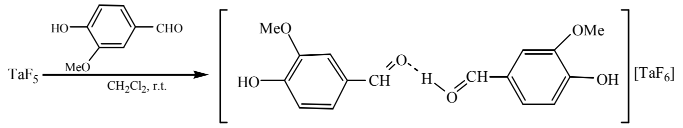
SCHEME 1

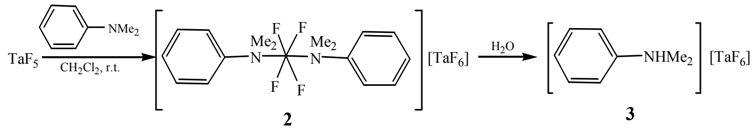
Reaction of TaF_5 with vanillin.



1

SCHEME 2

Reaction of TaF_5 with N,N-dimethylaniline.



2

3

Captions for Figures and Tables

Figure 1. ORTEP representation of the content of the asymmetric unit of the unit cell of $\{[4\text{-}(OH)\text{-}3\text{-}(OCH_3)C_6H_3CH(=O\text{–}H)][4\text{-}(OH)\text{-}3\text{-}(OCH_3)C_6H_3CHO]\}[TaF_6]$, **1**, with key atoms labeled. Displacement ellipsoids are at the 50% probability level.

Figure 2. The H-bonded dimeric $\{[4\text{-}(OH)\text{-}3\text{-}(OCH_3)C_6H_3CH(=O\text{–}H)][4\text{-}(OH)\text{-}3\text{-}(OCH_3)C_6H_3CHO]\}^+$ cation present in **1**. The dashed line represents the O(6)-H(6)···O(3) hydrogen bond.

Table 1. Main bond distances (Å) and angles (°) of **1**.

Table 2. Hydrogen bonds for **1** [Å and °]

Table 3. Crystal data and details of the structure refinement for **1**.

TABLES

Table 1. Main bond distances (Å) and angles (°) of **1**.

$\{[4\text{-(OH)-3-(OCH}_3)C_6H_3CH(=O–H)][4\text{-(OH)-3-(OCH}_3)C_6H_3CHO)]\}^+$ cation			
C(1)–C(2)	1.41(3)	C(11)–C(12)	1.35(3)
C(2)–C(3)	1.36(3)	C(12)–C(13)	1.39(3)
C(3)–C(4)	1.41(3)	C(13)–C(14)	1.38(3)
C(4)–C(5)	1.46(3)	C(14)–C(15)	1.40(3)
C(5)–C(6)	1.30(3)	C(15)–C(16)	1.34(3)
C(1)–C(6)	1.42(3)	C(11)–C(16)	1.46(3)
C(4)–C(8)	1.39(3)	C(14)–C(18)	1.47(3)
C(1)–O(1)	1.34(2)	C(11)–O(4)	1.34(3)
C(6)–O(2)	1.38(2)	C(16)–O(5)	1.37(2)
C(8)–O(3)	1.26(2)	C(18)–O(6)	1.22(2)
C(7)–O(2)	1.50(2)	C(17)–O(5)	1.42(2)
O(3)–C(8)–C(4)	119.9(19)	O(6)–C(18)–C(14)	124(2)
$[TaF_6]^-$ anion			
Ta(1)–F(1)	1.886(18)	Ta(1)–F(2)	1.81(2)
Ta(1)–F(3)	1.857(18)	Ta(1)–F(4)	1.846(19)
Ta(1)–F(5)	1.85(2)	Ta(1)–F(6)	1.90(2)
F(5)–Ta(1)–F(3)	170.7(9)	F(2)–Ta(1)–F(1)	178.4(9)
F(4)–Ta(1)–F(6)	177.6(10)		

Sum angles at C(1): 360(3)°; Sum angles at benzene ring; 720(4)°.

Table 2. Hydrogen bonds for **1** [Å and °]

D-H···A	**d(D-H)**	**d(H···A)**	**d(D···A)**	**<(DHA)**
O(1)-H(1)···O(4)#1	0.84	2.04	2.754(15)	143.2
O(1)-H(1)···O(2)	0.84	2.15	2.610(18)	114.2
O(4)-H(4)···F(5)#2	0.84	2.07	2.91(3)	176.1
O(6)-H(6)···O(3)#1	0.84	1.64	2.48(2)	171.8

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,y-1/2,z #2 -x+3/2,y+1/2,z

Table 3. Crystal data and details of the structure refinement for **1**.

Formula	$C_{16}H_{17}F_6O_6Ta$
Fw	600.25
T, K	100(2)
λ, Å	0.71073
Crystal system	Orthorhombic
Space Group	*Pbca*
a, Å	13.284(6)
b, Å	16.258(7)
c, Å	17.939(8)
Cell Volume, Å^3	3874(3)
Z	8
D_c, g cm^{-3}	2.058
μ, mm^{-1}	5.761
F(000)	2304
Crystal size, mm	0.18×0.16×0.10
θ limits, °	2.27–25.03
Reflections collected	26350
Independent reflections	3409 [R_{int} = 0.1391]
Data / restraints /parameters	3409/ 170 / 262
Goodness on fit on F^2	1.173
R_1 ($I > 2\sigma(I)$)	0.1004
wR_2 (all data)	0.2535
Largest diff. peak and hole, e Å^{-3}	2.749 / –3.098

Figure 1

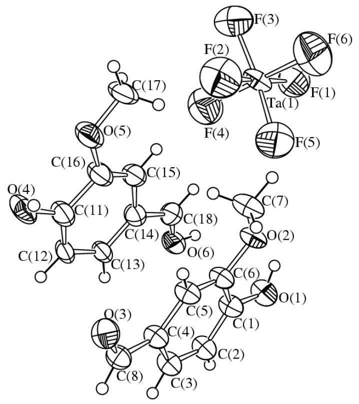


Figure 2