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Structural Characterization of a Fluorido-Amide of Niobium, and Facile CO2 Incorporation Affording a Fluorido-Carbamate

--Manuscript Draft--

Abstract:	The first compounds of niobium(V) with fluorido and monodentate amido ligands, 1a-c, are tetranuclear cations which were formed by the reaction between NbF5 and Me3SiNMe2, in the presence of a chloride (or bromide) source. The fluorido/carbamato derivative NbF2(O2CNMe2)3, 2, was obtained in good yields from NbF5/Me3SiNMe2, in the presence of carbon dioxide at 1 atm pressure and ambient temperature. All the products were characterized by analytical and spectroscopic (IR, multinuclear NMR) methods, and by X-ray diffraction in the cases of 1b-c. DFT calculations were useful to elucidate the structures of the products, and to give insight into the reaction pathways.

Author Comments:	To the Editor Eur. J. Inorg. Chem. Pisa, 2017 November 7 Dear Editor, please find uploaded the manuscript: "Structural Characterization of a Fluorido-Amide of Niobium, and Facile CO2 Incorporation Affording a Fluorido-Carbamate" by G. Bresciani, M. Bortoluzzi, S. Zacchini, F. Marchetti and G. Pampaloni that we would like to be considered for publication in European Journal of Inorganic Chemistry as a Paper. We repute this manuscript suitable to publication for the following reasons: 1) The coordination chemistry of niobium pentafluoride has represented an intensively

investigated field of research (see for instance: Angew. Chem. Int. Ed. 2014, 53, 5431; Dalton Trans., 2014, 43, 9557; Chem. Soc. Rev., 2013, 42, 1460; Chem. Eur. J. 2013, 19, 13962).

2) Several coordination compounds of MF_5 (M = Nb, Ta) have been reported in the last decade, while amides are versatile ligands which have been used to prepare a range of metal complexes for applications in catalysis and material chemistry. Despite this preamble, fluorido-amides of niobium or tantalum remain a substantially unknown family of inorganic compounds.

3) We report the synthetic procedure to fluorido-amido compounds of niobium, from NbF_5 and Me_3SiNMe_2. The products share the same structural motif, i.e. a tetranuclear niobium frame.

4) We demonstrate that the NbF_5/Me_3SiNR_2 reaction systems efficiently absorb CO_2 to produce fluorido-carbamato derivatives. The first example of a Nb fluorido-carbamate, being also a very rare example of metal fluorido-carbamate in general, has been obtained. Its structure has been elucidated by spectroscopic methods and with the assistance of DFT calculations.

I hope that the manuscript will be considered acceptable for publication in the European Journal of Inorganic Chemistry.

Yours sincerely,

Guido Pampaloni

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FULL PAPER _____

Structural Characterization of a Fluorido-Amide of Niobium, and Facile CO_2 Incorporation Affording a Fluorido-Carbamate

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The first compounds of niobium(V) with fluorido and monodentate amido ligands, **1a-c**, are tetranuclear cations which were formed by the reaction between NbF_5 and Me_3SiNMe_2, in the presence of a chloride (or bromide) source. The fluorido/carbamato derivative $NbF_2(O_2CNMe_2)_3$, **2**, was obtained in good yields from NbF_5/Me_3SiNMe_2, in the presence of carbon dioxide at 1 atm pressure and ambient temperature. All the products were characterized by analytical and spectroscopic (IR, multinuclear NMR) methods, and by X-ray diffraction in the cases of **1b-c**. DFT calculations were useful to elucidate the structures of the products, and to give insight into the reaction pathways.
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Introduction

For reasons clearly defined in a recent review by Levason and co-workers, the coordination chemistry of transition metal fluorides was neglected for many years and, when complexes were reported, the characterizations were often poor, and the properties not investigated in detail.[1]

In spite of this preamble, the interest in high valent fluorides of groups 4 and 5 metals has progressively grown in the last decade, due to possible applications in organic synthesis,[2] in material chemistry[3] and as possible precursors of innocent, weakly coordinating anions.[4] In particular, a variety of derivatives have been obtained and characterized from the reactions of easily available niobium and tantalum pentafluorides, MF_5 (M = Nb, Ta), with *N*-,[5] *O*-,[6] *S*-donors,[7] and with phosphines and arsines.[5a,8]

To date, this flourishing investigation has not led to the synthesis of ternary fluorido-amides of niobium or tantalum,[9] which remain a substantially unknown family of inorganic compounds.[10,11] Few relevant, well characterized species comprise the amido unit as part of a pincer multidentate frame[12] and/or additional ligands.[13]

The availability of Nb/Ta fluorido-amides may be desirable also since amides are versatile ligands providing to the resulting metal complexes suitable properties for a possible use in catalysis[14] or in the formation of thin films of the metal[15] or the metal oxide.[16]cyclic esters, other than alkenes.[17]

The absence of information of niobium and tantalum fluorido-amides reflects the curious paucity of reports in the literature on the reactivity of the related pentafluorides with aliphatic amines.[18] Otherwise, the parallel reactivity of MCl_5 (M = Nb, Ta) with various amines has been exhaustively investigated, providing in some cases a route to chlorido-amido compounds.[19] More typically, the synthetic method to access M(V) dialkylamides (M = Nb, Ta) consists in the metathesis reaction between $NbCl_5$ and an alkali metal salt of the amido anion.[20] Then, a variety of amido derivatives can be obtained from $M(NR_2)_5$, thanks to the easy displacement of a light amido unit as volatile dialkyamine.[20c,21]

In this setting, we decided to explore the possibility of preparing niobium(V) compounds with fluorido- and dialkylamido ligands, according to a strategy (use of an organic trimethylsilyl reactant) successfully employed for the synthesis of fluorido-alkoxido[6b] and fluorido-azido[5b,d] complexes. The structural characterization of the first ternary fluorido-amide of niobium is presented. Furthermore, we demonstrate that the NbF_5/trimethylsilylamine system efficiently captures CO_2 in mild conditions and, thus, can be used as a convenient precursor to unprecedented metal fluorido-carbamates.

Results and Discussion

A suspension of NbF_5 in toluene reacted smoothly with 5 equivalents of Me_3SiNMe_2 at room temperature to afford a complex solid mixture. After extraction with $CHCl_3$, an extremely moisture sensitive compound was isolated and identified as $[Nb_4F_6(NMe_2)_{12}][Cl]_2$, **1a**, on the basis of spectroscopic (multinuclear NMR) and analytical data, including Cl elemental

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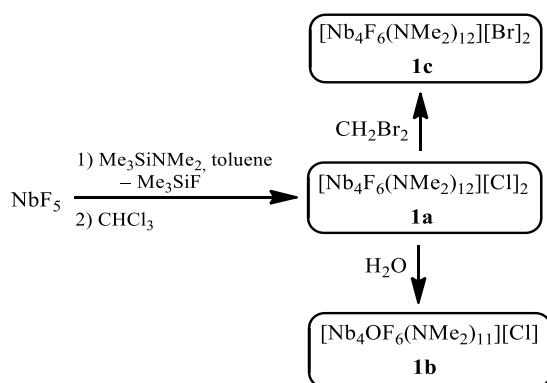[b] CIRCC, via Celso Ulpiani 27, I-70126 Bari, Italy.
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analysis, and X-ray characterization of a related compound (**1b**, vide infra). When different stoichiometric ratios were employed, **1a** was finally isolated as the prevalent product, although in lower yields.

$$[Nb_4F_6(NMe_2)_{12}][Br]_2$$
1c

$$\uparrow CH_2Br_2$$

$$NbF_5 \xrightarrow[\substack{1)\ Me_3SiNMe_2,\ toluene \\ -\ Me_3SiF \\ 2)\ CHCl_3}]{} [Nb_4F_6(NMe_2)_{12}][Cl]_2$$
1a

$$\downarrow H_2O$$

$$[Nb_4OF_6(NMe_2)_{11}][Cl]$$
1b

Scheme 1. Formation of fluoride-amido complexes from NbF_5.

The NMR spectra (^1H, ^{13}C, ^{19}F and ^{93}Nb) of **1a** ($CDCl_3$ solution) are all featured by a single resonance, thus suggesting a rather symmetrical structure; the singlet at −158 ppm in the ^{19}F NMR spectrum indicates the presence of bridging fluorine atoms.[6b]

The isolation of **1a** as a chlorido salt starting from NbF_5 is rather surprising. We suggest that the chloroform used for the recrystallization acts as a chlorido source, indeed similar examples where chloroform behaves as a Cl-donor are documented.[22]

Single X-ray quality crystals of different nature were obtained either when **1a** was dissolved in $CDCl_3$ in the presence of CH_2Br_2 added for analytical purposes (**1c**), or from a $CHCl_3$/pentane mixture (**1b**).

Crystals of **1c** correspond to $[Nb_4F_6(NMe_2)_{12}][Br]_2\cdot 8CHCl_3$ (Figure 1 and Table 1), the bromide anions being reasonably generated by halide exchange between **1a** and dibromomethane. Actually, examples of haloalkane activation by early transition metal complexes are known.[23]

The $[Nb_4F_6(NMe_2)_{12}]^{2+}$ cation in **1c·8CHCl₃** represents the first structurally characterized ternary compound of a group 5 metal with fluorido and monodentate amido ligands. The structure may be viewed as composed of four identical *fac*-$NbF_3(NMe_2)_3$ octahedra condensed *via* the triangular F_3-faces. This results in a Nb_4 tetrahedron whose six edges are bridged by six μ-F ligands. A similar $M_4(\mu$-F$)_6$ core is present in $[Ti_4(\mu$-F$)_6F_{12}]^{2-}$,[24] $[W_4(\mu$-F$)_6F_{12}]^{2-}$,[25] and $[Al_4(\mu$-F$)_6F_{12}]^{6-}$.[26] The μ-F bridges are perfectly symmetric and all the Nb–F [4c,27] and Nb–NMe_2[28] distances are as expected for octahedral Nb(V) complexes. The Nb–F–Nb bridges [156.12(9)-157.34(9)°] are considerably bended in view of the tetrahedral structure of the Nb_4 cage, as previously found in the $[NbF_2(\mu$-F$)(OPh)_2]_3$ trimer.[6b] Otherwise almost linear Nb–F–Nb interactions [182.5°] are observable within the tetrameric $[NbF_5]_4$.[29] Some H-bonds are present within the crystal structure of **1c·8CHCl₃**, involving the Br⁻ anions and the $CHCl_3$ solvent molecules.

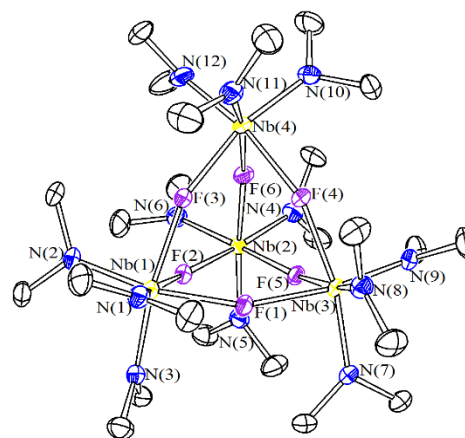**Figure 1.** View of the cation $[Nb_4F_6(NMe_2)_{12}]^{2+}$ in $[Nb_4F_6(NMe_2)_{12}]Br_2$, **1c**, with key atoms labelled. Displacement ellipsoids are at the 50% probability level. H-atoms have been omitted for clarity.

Table 1. Selected bond distances (Å) and angles (°) for **1c**.

Nb(1)–F(1)	2.1248(16)	Nb(1)–N(1)	1.961(3)
Nb(1)–F(2)	2.1137(17)	Nb(1)–N(2)	1.964(2)
Nb(1)–F(3)	2.1222(17)	Nb(1)–N(3)	1.952(3)
Nb(2)–F(2)	2.1235(17)	Nb(2)–N(4)	1.958(3)
Nb(2)–F(5)	2.1108(16)	Nb(2)–N(5)	1.957(3)
Nb(2)–F(6)	2.1184(16)	Nb(2)–N(6)	1.965(3)
Nb(3)–F(1)	2.1154(16)	Nb(3)–N(7)	1.962(2)
Nb(3)–F(4)	2.1177(16)	Nb(3)–N(8)	1.962(3)
Nb(3)–F(5)	2.1153(16)	Nb(3)–N(9)	1.954(3)
Nb(4)–F(3)	2.1160(17)	Nb(4)–N(10)	1.949(3)
Nb(4)-F(4)	2.1092(16)	Nb(4)–N(11)	1.961(3)
Nb(4)–F(6)	2.1162(17)	Nb(4)–N(12)	1.961(3)
Nb(1)–F(1)–Nb(3)	156.12(9)	Nb(1)–F(2)–Nb(2)	157.13(9)
Nb(1)–F(3)–Nb(4)	157.34(9)	Nb(3)–F(4)–Nb(4)	156.68(9)
Nb(2)–F(5)–Nb(3)	156.97(9)	Nb(2)–F(6)–Nb(4)	157.32(9)

Attempts to crystallize **1a**, *i.e.* the product of the reaction of NbF_5 with Me_3SiNMe_2 treated with $CHCl_3$ but in the absence of bromide source (Scheme 1), led us to the isolation of few crystals corresponding to **1b**. The structural analysis (Figure 2 and Table 2) revealed that **1b** had the composition $[Nb_4OF_6(NMe_2)_{11}]Cl\cdot 4CHCl_3$, the $[Nb_4OF_6(NMe_2)_{11}]^+$ cation being closely related to the $[Nb_4F_6(NMe_2)_{12}]^{2+}$ cation of **1c**. The former cation is probably generated from the latter by means of water traces present in the solvents used for the crystallization procedure. The structural characterization of **1b** constitutes indirect proof for the identity of **1a**, and confirms the tendency of Nb(V) fluoride amido compounds to adopt the tetranuclear frame. In **1b**, the unique terminal F(1) ligand is bonded to Nb(1) in *trans* position respect to the μ-O(1) ligand. As for **1c**, the Nb–F–Nb bridges are symmetric, whereas a considerable asymmetry is present in the Nb(1)–O(1)–Nb(2) oxido-bridge. Thus, the Nb(1)–O(1) interaction [1.832(4) Å] is rather shorter than Nb(2)–O(1) [2.042(4) Å], suggesting that the oxido bridge might be better described as a Nb=O–Nb interaction. Some H-bonds are present within the crystal structure of **1b·4CHCl₃** involving the Cl⁻ anion and the $CHCl_3$ lattice molecules.
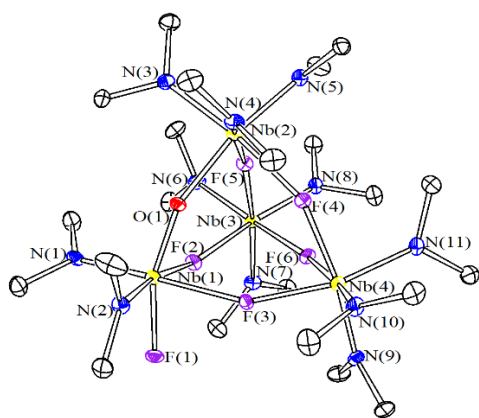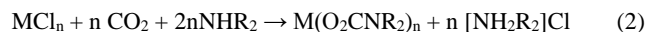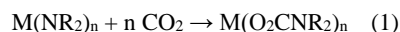
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Figure 2. View of the cation $[Nb_4OF_6(NMe_2)_{11}]^+$ in $[Nb_4OF_6(NMe_2)_{11}]Cl$, **1b** with key atoms labelled. Displacement ellipsoids are at the 50% probability level. H-atoms have been omitted for clarity.

**Table 2.** Selected bond distances (Å) and angles (°) for **1b**.

Nb(1)–F(2)	2.137(4)	Nb(1)–F(1)	1.974(4)
Nb(1)–F(3)	2.174(4)	Nb(1)–N(1)	1.977(6)
Nb(1)–O(1)	1.832(4)	Nb(1)–N(2)	1.973(5)
Nb(2)–O(1)	2.042(4)	Nb(2)–N(3)	1.972(6)
Nb(2)–F(4)	2.148(4)	Nb(2)–N(4)	1.977(6)
Nb(2)–F(5)	2.139(4)	Nb(2)–N(5)	1.990(6)
Nb(3)–F(2)	2.095(4)	Nb(3)–N(6)	1.955(6)
Nb(3)–F(5)	2.097(4)	Nb(3)–N(7)	1.963(6)
Nb(3)–F(6)	2.106(3)	Nb(3)–N(8)	1.955(6)
Nb(4)–F(3)	2.065(4)	Nb(4)–N(9)	1.958(6)
Nb(4)–F(4)	2.095(4)	Nb(4)–N10)	1.948(5)
Nb(4)–F(6)	2.131(3)	Nb(4)–N(11)	1.959(6)
Nb(1)–O(1)–Nb(2)	158.4(3)	Nb(1)–F(2)–Nb(3)	148.45(19)
Nb(1)–F(3)–Nb(4)	150.43(18)	Nb(2)–F(5)–Nb(3)	155.25(18)
Nb(2)–F(4)–Nb(4)	153.67(19)	Nb(3)–F(6)–Nb(4)	156.2(2)

It is well known that the reactions of dialkylamides of a wide range of metals, $M(NR_2)_n$, with CO_2 can afford homoleptic carbamato complexes (Eq. 1).[30] These complexes can be prepared also by a straightforward synthetic route starting from easily available metal chlorides (Eq. 2).[31]

$$M(NR_2)_n + n\ CO_2 \rightarrow M(O_2CNR_2)_n \quad (1)$$

$$MCl_n + n\ CO_2 + 2nNHR_2 \rightarrow M(O_2CNR_2)_n + n\ [NH_2R_2]Cl \quad (2)$$

Metal carbamates constitute an intriguing class of compounds, which have revealed to be suitable precursors to homogeneous catalysis,[32] chemical vapour deposition [33] and material chemistry.[34] There is a current interest in expanding the family of metal-carbamato complexes to mixed halido-carbamates. For instance, metal chlorido-carbamates may exhibit better activities in catalytic processes, compared to the respective homoleptic species.[32c] Until today, the unique case of a fluorido-carbamato complex, i.e. $TiF_2(O_2CNEt_2)_2$, has been obtained by metathesis reaction between TiF_4 and the homoleptic carbamate $Ti(O_2CNEt_2)_4$.[35]

These observations prompted us to investigate the reactivity of the newly prepared fluorido-amido complexes of Nb(V) with carbon dioxide.

The optimized conditions to obtain the final fluorido carbamato species consisted in performing the reaction of NbF_5 with 5 equivalents of Me_3SiNR_2 (R = Me, Et) directly under a carbon dioxide atmosphere (p = 1 atm, RT). Using these conditions, the complex $NbF_2(O_2CNMe_2)_3$, **2**, was afforded in high yield. On the other hand, a mixture of products was produced from NbF_5/Me_3SiNEt_2, Scheme 2.
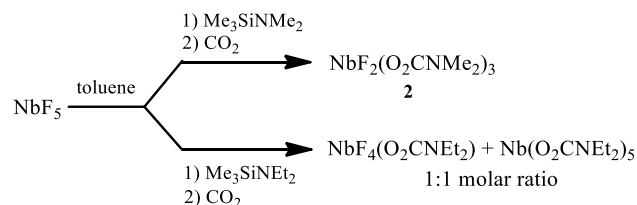
Scheme 2. Reactions of NbF_5 with Me_3SiNR_2 (R = Me, Et) under a CO_2 atmosphere.

Compound **2** was fully characterized by elemental analysis and IR and multinuclear NMR spectroscopy. The IR spectrum shows a diagnostic, strong absorption at 1625 cm^{-1} which is indicative of a carbamato ligand bonded to a metal with monodentate mode.[36] The ^{19}F NMR spectrum exhibits two resonances at 128 and 121 ppm, in agreement with the presence of two non-equivalent terminal fluorine atoms. Instead the ^{93}Nb NMR consists of a unique resonance centred at -1039 ppm.

We were not able to grow single crystals of **2**, thus the presumable structure of this compound was modelled by DFT calculations upon consideration of several possible structures. The most stable ground-state geometry, depicted in Figure 3, shows a distorted octahedral configuration, with the fluorine atoms in mutual *cis* position, two $[O_2CNMe_2]^-$ ligands κ^1O-bonded and the third one acting as *O,O* bidentate. The isomer bearing *trans*-fluorido ligands resulted less stable by about 3.5 kcal mol^{-1} (enthalpy variation).
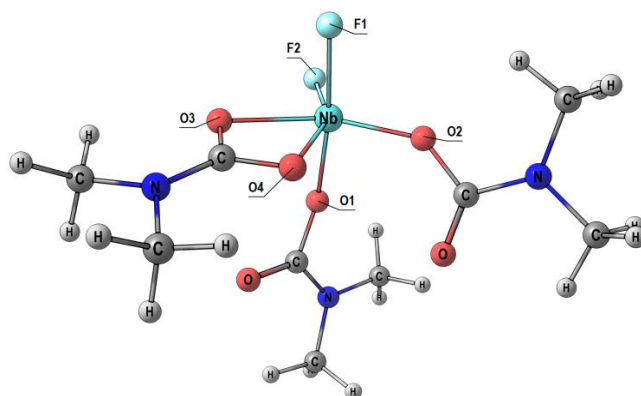

Figure 3. DFT-optimized geometry of **2** (C-PCM/ωB97X calculations). Selected computed bond lengths (Å): Nb−F1 1.890, Nb−F2 1.871, Nb−O1 1.912, Nb−O2 1.905, Nb−O3 2.103, Nb−O4 2.111. Selected computed angles (°): F1−Nb−F2 91.2, F1−Nb−O1 172.3, F1−Nb−O2 92.2, F1−Nb−O3 86.5, F1−Nb−O4 87.0, F2−Nb−O1 91.8, F2−Nb−O2 118.7, F2−Nb−O3 92.0, F2−Nb−O4 153.6, O1−Nb−O2 92.6, O1−Nb−O3 86.3, O1−Nb−O4 87.2, O2−Nb−O3 149.3, O2−Nb−O4 87.7.

The reaction of NbF_5 with Me_3SiNEt_2/CO_2, using three equivalents of *N,N*-trimethylsilylamine, afforded a mixture of products, containing $Nb(O_2CNEt_2)_5$ and $NbF_4(O_2CNEt_2)$, according to the merging of analytical and spectroscopic data [^{93}Nb NMR: two resonances at −1365 and −1029 ppm; ^{19}F NMR: one resonance at 125.6 ppm; ^{13}C NMR: resonances due to $Nb(O_2CNEt_2)_5$, at 167.7 (C=O), 39.8 (CH$_2$), 13.5 ppm (CH$_3$)].[37] We calculated the enthalpy variations for the ligand exchange reactions reported in Eq. 3. They are slightly negative and very similar to each other (R = Me: −8.6 kcal mol^{-1}; R = Et: −8.2 kcal mol^{-1}).

$$2\ NbF_2(O_2CNR_2)_3 \rightarrow Nb(O_2CNR_2)_5 + NbF_4(O_2CNR_2) \quad (3)$$
$$(R = Me, Et)$$
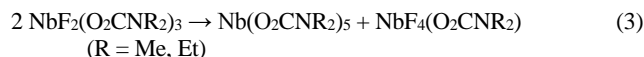
On account of the calculated thermochemical parameters, the different outcomes reported in Scheme 2 are probably ascribable to the insolubility of **2** in aromatic and aliphatic solvents (see Experimental), favouring its successful and clean isolation.

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Conclusions

The reaction of NbF_5 with N,N-dimethyltrimethylsilylamine has led us to the structural characterization of the first ternary niobium fluorido-amide. The introduction of a chloride (or bromide) source seems crucial to allow the stabilization and the isolation of a favourite cationic tetra-niobium motif. Moreover, NbF_5/trimethylsylilamine reaction mixtures behave as efficient CO_2 trapping systems, leading to the formation of niobium fluorido-carbamato derivatives via CO_2 fixation. The successful isolation of these products, representing very rare examples of mixed metal fluorido-carbamates, becomes viable when their solubility characteristics permit the efficient separation from the reaction media.

Experimental

General

***Warning*. The metal products reported in this paper are highly moisture-sensitive, thus they were stored in sealed glass tubes under nitrogen or argon once obtained, and rigorously anhydrous conditions were required for the reaction and crystallization procedures.** All the operations were carried out under an atmosphere of prepurified argon. The glass reaction vessels were oven dried at 140 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. Solvents (Sigma Aldrich) and diethylamine (Sigma Aldrich, 99.5%) were distilled from appropriate drying agents before use. N,N-dialkyl-1,1,1,-trialkylsilylamines (Sigma Aldrich, 97%), NbF_5 [29] (Strem, 99.5%) was stored under argon atmosphere as received. Infrared spectra were recorded at 298 K on a FTIR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. ^{1}H, ^{13}C, ^{19}F, ^{51}V and ^{93}Nb NMR spectra were recorded at 298 K with a Bruker Avance II DRX 400 spectrometer. The chemical shifts for ^{1}H and ^{13}C were referenced to the non-deuterated aliquot of the solvent; the chemical shifts for ^{93}Nb were referenced to external $[NEt_4][NbCl_6]$; the chemical shifts for ^{19}F were referenced to external $CFCl_3$.

C, H, N analyses were performed on a Carlo Erba mod. 1106 instrument. The chloride content was determined by the Volhard method [38] on samples prepared by dissolution of the solid in aqueous Na_2CO_3 at boiling temperature, followed by cooling to room temperature and addition of HNO_3 up to acidic pH. Niobium was analyzed as Nb_2O_5, obtained by hydrolysis of the samples followed by calcination in a platinum crucible.

Synthesis of $[Nb_4F_6(NMe_2)_{12}][X]_2$ (X = Cl, 1a; Br, 1b).

Me_3SiNMe_2 (0.34 mL, 2.1 mmol) was added to a suspension of NbF_5 (0.08 g, 0.42 mmol) in toluene (5 mL). The reaction mixture was stirred for 20 hours at room temperature. The volatiles were removed in vacuo and the residue was treated with pentane (2 × 10 mL) and then dried in vacuo. An orange, extremely hygroscopic solid was obtained. Yield: 0.10 g. ^{1}H NMR ($CDCl_3$) δ = 3.75 (s), 3.69-3.49 (m-br), 2.55 (s), 2.33 (s) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 51.0, 50.3, 49.6 ppm. ^{93}Nb{^{1}H} NMR ($CDCl_3$) δ = −253, −612, −921, −1550 (m, $[NbF_6]^-$) ppm. Dissolution in $CHCl_3$ followed by slow evaporation of the solvent afforded 0.05 g (45% yield based on niobium) of $[Nb_4F_6(NMe_2)_{12}]Cl_2$, **1a**, as yellow crystalline solid. Anal. Calc. for $C_{24}H_{72}Cl_2F_6N_{12}Nb_4$: C, 26.56; H, 6.68; N, 15.48; Nb, 34.24; Cl, 6.53. Found: C, 26.06; H, 6.48; N, 15.08; Nb, 33.84; Cl, 6.44. ^{1}H NMR ($CDCl_3$) δ = 3.70 (s, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 50.3 (CH_3) ppm. ^{19}F{^{1}H} NMR ($CDCl_3$) δ = −158 (s, $F_{bridging}$) ppm. ^{93}Nb{^{1}H} NMR ($CDCl_3$) δ = −250 (Δν½ = 1.4×10^3 Hz) ppm.

Crystallization of **1a** from chloroform / pentane mixture at 243 K afforded pale yellow crystals of $[Nb_4F_5(\mu\text{-}O)(NMe_2)_{12}][Cl]$, **1b**, in two weeks. Anal. Calc. for $C_{24}H_{72}ClF_5N_{12}ONb_4$: C, 27.53; H, 6.93; N, 16.05; Cl, 3.39. Found: C, 27.16; H, 6.29; N, 15.78; Cl, 3.25. A single crystal was used for a X-ray diffraction analysis.

In a different preparation, few crystals of $[Nb_4F_6(NMe_2)_{12}][Br]_2$, **1c**, were obtained by cooling (243 K) a saturated $CDCl_3$ solution of **1a** in the presence of CH_2Br_2. A single crystal was used for a X-ray diffraction analysis.

Synthesis of $NbF_2(O_2CNMe_2)_3$, 2.

A suspension of NbF_5 (0.12g; 0.64 mmol) in toluene (50 ml) was treated with Me_3SiNMe_2 (0.20 g, 1.96 mmol), The mixture was stirred for 24 hours at room temperature and then saturated with CO_2. After 24 hours under CO_2 atmosphere, a clear solution was obtained. The solvent was partially removed in vacuo and the residue

was treated with pentane (15 mL). The solid was recovered by filtration and dried in vacuo affording $NbF_2(O_2CNMe_2)_3$, **2** (0.214 g, 85% yield) as a highly moisture sensitive, microcrystalline solid. Anal. Calc. for $C_9H_{18}F_2N_3O_6Nb$: C, 27.35; H, 4.59; N, 10.63; Nb, 23.51. Found: C, 27.01; H, 4.68; N, 10.48; Nb, 23.24. IR (solid state) ν = 2955vw, 2874vw, 2782vw, 1626vs (C=O), 1463m, 1445m, 1415s, 1059w, 1028w, 952w-m, 875w-m, 863w-m, 675vsm^{-1}. ^{1}HNMR ($CDCl_3$) δ = 3.01 (s, CH_3), 3.00 (s, CH_3) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 168.8 (C=O), 168.1 (C=O), 34.9 (CH_3), 34.5 (CH_3) ppm. ^{19}F{^{1}H} NMR (400 MHz, $CDCl_3$) δ = 128 (s), 121 (s) ppm. ^{93}Nb{^{1}H} NMR ($CDCl_3$) δ = −1039 (Δν½ = 4.2×10^3 Hz) ppm.

Reaction of NbF_5 with Me_3SiNEt_2.

A suspension of NbF_5 (0.30 g, 1.62 mmol) in toluene (20 ml) was treated with Me_3SiNEt_2 (0.92 mL, 4.85 mmol). The mixture was stirred for 20 hours at room temperature. The argon atmosphere was replaced by CO_2. After stirring overnight at room temperature, the solvent was partially removed in vacuo and the residue was treated with pentane (30 mL). The solid was recovered by filtration and dried in vacuo affording a brown solid (0.403 g) extremely sensitive to moisture. The brown solid was identified as a ca. 1:1 mixture of $Nb(O_2CNMe_2)_5$ and $NbF_4(O_2CNMe_2)$. Anal. Calc. for $C_{30}H_{60}F_4N_6O_{12}Nb_2$: C, 37.58; H, 6.31; N, 8.77; Nb, 19.38. Found: C, 37.02; H, 6.67; N, 8.46; Nb, 18.99. IR (solid state) ν = 2976w, 2938w, 2877vw, 1584vs, br (C=O), 1482m, 1434s, 1381m, 1322s, 1261w, 1208m, 1091m, 983w, 931m, 839m-s, 782m.scm^{-1}. ^{1}HNMR ($CDCl_3$) δ = 3.44-3.34 (m, 2H, CH_2), 1.20-1.11 (m, 3 H, CH_3), ppm. ^{13}C{^{1}H} NMR ($CDCl_3$) δ = 168.3 (C=O), 167.7 (C=O), 39.8 (CH_2), 39.2 (CH_2), 13.5 (CH_3), 13.3 (CH_3) ppm. ^{19}F{^{1}H} NMR ($CDCl_3$) δ = 125.6 (s), ppm. ^{93}Nb{^{1}H} NMR ($CDCl_3$) δ = −1365 (Δν½ = 8.0×10^3 Hz), −1029 (Δν$^{1/2}$ = 5.3×10^3 Hz) ppm.

X-ray crystallography.

Crystal data and collection details for **1b·4CHCl$_3$** and **1c·8CHCl$_3$** are reported in Table 3. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a PHOTON100 detector using Mo–Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS). [39] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2. [40] Hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Table 3. Crystal data and experimental details for **1b·4CHCl$_3$** and **1c·8CHCl$_3$**.

	1b·4CHCl$_3$	1c·8CHCl$_3$
Formula	$C_{26}H_{70}Cl_{13}F_6N_{11}Nb_4O$	$C_{32}H_{80}Br_2Cl_{24}F_6N_{12}Nb_4$
Fw	1499.42	2129.34
T, K	100(2)	100(2)
λ, Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
, Å	10.329(3)	14.7404(6)
b, Å	15.147(4)	23.9630(9)
c, Å	20.309(6)	23.5127(9)
a, °	85.668(4)	90
β, °	76.703(4)	93.574(2)
g, °	74.623(4)	90
Cell Volume, Å^3	2981.2(14)	8289.1(6)
Z	2	4
D_c, g cm^{-3}	1.670	1.706
μ, mm^{-1}	1.384	2.324
F(000)	1500	4208
Crystal size, mm	0.220×0.160×0.110	0.180×0.160×0.120
θ limits, °	1.394–26.997	1.384–27.191
Reflections collected	28484	139233
Independent reflections	12796 [R_{int}=0.0523]	18238 [R_{int}=0.0589]
Data / restraints /parameters	12796 / 18 / 550	18238 / 240 / 780
Goodness of fit on F^2	1.132	1.013
R_1 ($I > 2\sigma(I)$)	0.0651	0.0325
wR_2 (all data)	0.1535	0.0746
Largest diff. peak / hole, e Å^{-3}	1.425 / −1.917	1.686 / −1.322

Computational studies

The computational geometry optimizations were carried out without symmetry constrains, using the hybrid-GGA EDF2 functional [41] in combination with the 6-31G** basis set (ECP-based LANL2DZ basis set for Nb). [42] The "restricted" formalism was always applied. The stationary points were characterized by IR simulations (harmonic approximation),

from which zero-point vibrational energies and thermal corrections (T = 298.15 K) were obtained.[43] Further optimization of selected geometries was carried out using the range-separated DFT functional ωB97X, [44] in combination with the split-valence polarized basis set of Ahlrichs and Weigend, with ECP for the niobium centre.[45] The C-PCM implicit solvation model was added to ωB97X calculations, considering chloroform as continuous medium.[46] The software used for C-PCM/ωB97X calculations was Gaussian '09, [47] while EDF2 calculations were performed with Spartan '16.[48]

Acknowledgements

Supplementary Material

Cartesian coordinates of all DFT-optimized compounds are collected in a separated .xyz file. CCDC reference numbers 1526864 (**1b·4CHCl₃**), 1526865 (**1c·8CHCl₃**), contain the supplementary crystallographic data for the X-ray studies reported in this paper. 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, CambridgeCB21EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

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The first fluorido/amido and fluorido/carbamato complexes of niobium have been obtained and fully characterized.

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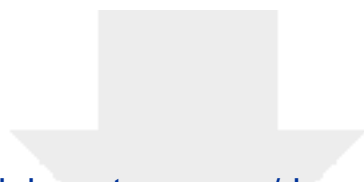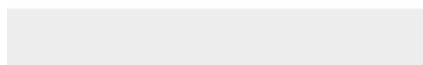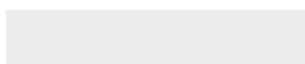**Structural Characterization of a Fluorido-Amide of Niobium, and Facile CO_2 Incorporation Affording a Fluorido-Carbamate**

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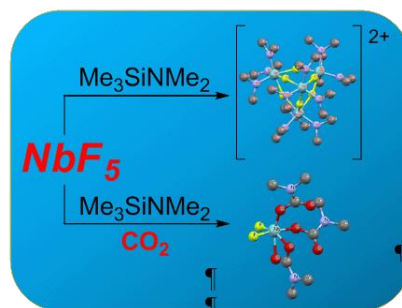
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