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Molecular niobium(V) complexes with mononuclear {Nb1} and dinuclear oxo species {Nb2O} connected through aryl di- or tetra-carboxylate linker

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Contribution from
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ABSTRACT: Several aryl polycarboxylic ligands (pyromellitic acid, 4,4'-azobenzenedicarboxylic acid and 3,3',5,5'-azobenzenetetracarboxylic acid) have been used to react with the pentavalent ethoxide niobium(V) precursor $Nb(OEt)_5$. Three new crystalline molecular compounds (**1** with pyromellitate, **2** with 4,4'-azobenzenedicarboxylate and **3** with 3,3',5,5'-azobenzenetetracarboxylate) were isolated from slow crystallization at room temperature from the mother liquid containing the precursor $Nb(OEt)_5$. They are composed of one polycarboxylate ligand fully coordinated to mononuclear or dinuclear octahedrally-coordinated niobium(V) units. For the dimers, the two adjacent niobium centers are bridged by one μ-O and one μ-OEt groups and complexed by only one of the syn-syn bidentate carboxylate function arms from the polytopic ligand. Compounds **1-3** were characterized in solid state by single-crystal and powder X-ray diffraction analysis. Insight into the formation of the three compounds was supported by the help of infrared and liquid ^{1}H NMR spectroscopy.

Keywords: niobium(V), polycarboxylic acid, coordination complex, single-crystal X-ray diffraction, NMR spectroscopy, infrared spectroscopy.

Introduction

Metal-Organic Frameworks (MOF) materials are actually intensively studied and represents a really important part of the metal carboxylate chemistry domain. These crystalline tridimensional assemblies are built up from inorganic cores linked to each other by organic ligands through M-O-C bonds. The incredible variety of these associations mainly comes from the library of commercially available and synthetic polytopic organic ligand and is only limited by the choice of the metallic elements necessary to build stable metal carboxylate linkages allowing the formation of the tridimensional materials. The metallic part of MOF compounds is generally constituted of divalent (ex: Zn^{2+}, Cu^{2+}, …), trivalent (Al^{3+}, Fe^{3+}, Cr^{3+}, … - also including lanthanides) or tetravalent cations (Ti^{4+}, Zr^{4+}, Ce^{4+}… - also including actinides). Only a few solids are related to higher valence cations[1]. For instance, uranyl chemistry related to the +6-oxidation state of uranium has led to a myriad of organic-inorganic networks. This is due to the specific double trans oxo ligand configuration of this element, corresponding to $\{UO_2\}^{2+}$, that makes it react more like a divalent cationic species[2]. The reactivity of high valence transition metals with carboxylic acids has been barely investigated, despite the occurrence of some complexes involving carboxylate ligands. In our laboratory, we were interested by the niobium(V) cation because its chemistry was reported in very rare occurrence, in the context of the synthesis of MOF compounds. For instance, recent works described the successful incorporation of niobium, as a doping element, into various well-known MOF archetypes such as MOF-5 (Nb(IV)[3], UiO-66 (Nb(V))[4], NU-1000 (Nb(V))[5] or CPO-27(Co) (Nb(V))[6], with the intent of studying properties in the catalysis field or the modification of electronic structures. As far as we known, the synthesis of niobium-based MOF structures has not been explored with carboxylate species as organic linkers. One can only encounter niobium in MOF-like systems as an oxyfluorinated $(NbOF_5)^{2-}$ basic building blocks in a mixed Nb(V)-Ni(II) square network (KAUST-7) with pyrazine ligands[7] or as mononuclear Nb(V)-node in a honeycomb lattice with 3,6-dichloro-2,5-dihydroxybenzoquinone ligand[8].

Nevertheless, if we consider molecular entities, several complexes of niobium stabilized by carboxylate molecules have been discovered. It can be found as a commercial precursor in a discrete Nb-centered mononuclear unit, when precipitated by oxalic acid to give either identified [A][NbO(C$_2$O$_4$)$_2$(H$_2$O)$_2$]·xH$_2$O (A = NH$_4^+$ [9,10] or Cs$^+$ [11]) or [A]$_3$[NbO(C$_2$O$_4$)$_3$]·xH$_2$O (A = NH$_4^+$ [12] or Rb$^+$ [13]) salts, which can be further associated with various pyridine-based molecules (phenanthroline, bipyridine, etc…)[14] or divalent transition metals complexes with [Zn(bpy)]$^{2+}$ [15], [Co(terpy)]$^{2+}$ [16], including a series [(Fe-Zn)(bpy)]$^{2+}$ [17] (bpy = 2,2'-bipyridine, terpy = 2,2':6',2''-terpyridine), or with rare-earth cations[18]. Other niobium oxalates have been identified in the presence of divalent counter cations such as barium in [Ba$_2$(H$_2$O)$_5$][NbO(C$_2$O$_4$)$_3$][HC$_2$O$_4$]·H$_2$O[19] or with peroxide groups[12]. The occurrence of peroxo-niobium centers are also encountered in a series of complexes involving citrate, tartrate, ethylenediaminetetra-acetate (edta) and propylenediaminetetra-acetate (pdta) ligands[20–22]. The other types of niobium-centered complexes have been isolated starting from niobium pentachloride or niobium alkoxides precursors.

The halide precursors reactivity was tested using the benzoic acid ligand (HO$_2$C-C$_6$H$_5$). It gave rise to the formation of two molecular dinuclear complexes, in which the niobium centers are bridged through the carboxylate arm of the monotopic benzoate molecules. In the first case, the dimer [Nb$_2$Cl$_6$(O$_2$C-C$_6$H$_5$)$_2$O][23] also showed one additional μ-oxo group bridging the two niobium centers, whereas it does not exist in the second dimer [Nb$_2$Cl$_4$(OEt)$_4$(O$_2$C-C$_6$H$_5$)$_2$][24]. Other benzoate derivatives (O$_2$C-R where R = FC$_6$H$_4$, p-ClC$_6$H$_4$, p-IC$_6$H$_4$, p-MeC$_6$H$_4$) are also mentioned in the work of Brown et al[24–26]. In this series, the addition of ethanol solvent to the initial solution led to the exchange of some chloride anions by ethoxy (OEt) groups, which stabilized this specific configuration without any central bridging μ-oxo group. A related dinuclear complex has also been identified with fluorosubstituted benzoate linker (O$_2$C-C$_6$F$_5$) for the purely chloride salt [Nb$_2$Cl$_8$(O$_2$C-C$_6$F$_5$)$_2$][25].

The chemical synthetical pathway using of metal alkoxides (M(OR)$_n$, where R= Me for methoxide, OEt for ethoxide, etc) has been more intensely studied, since these metalorganic compounds are known for their utilization as precursors for the elaboration of ceramics [27,28,29,30] and the substitution of a bidentate ligand can contribute to the alteration and modification of its properties [31,32,33,34,35,36]. Regarding the chemistry of niobium alkoxides, many complexes have been identified with monocarboxylic acids and are related to different niobium nuclearities. The alkoxide route allowed for the identification of a dinuclear niobium-centered complex [Nb$_2$O(O$_{Nep}$)$_6$(piv)$_2$] (where O$_{Nep}$ = OCH$_2$CMe$_3$ or Neopentanoxy) in the presence of pivalic acid (Me$_3$C-CO$_2$H = Hpiv). Its structure is related to the dimer [Nb$_2$Cl$_6$(O$_2$C-C$_6$H$_5$)$_2$O][26] obtained from the halide route, with two carboxylate arms from pivalate ligand and one bridging μ-oxo group. Here, the chloro anions are substituted by the neopentanoxy groups. However, in the same system, when using the terbutylacetic acid (Me$_3$C-CH$_2$-CO$_2$H = HtBAc), a higher condensed complex has been isolated with four niobium centers placed in a square configuration, and connected to four μ-oxo groups [Nb$_4$O$_4$(O$_{Nep}$)$_8$(tBAc)$_4$]. This dimeric moiety can be seen as the association of the two previously described dinuclear bricks [Nb$_2$O(O$_{alkoxide}$)$_3$(carboxylate)$_2$] linked to each other by two additional μ-oxo groups. Indeed, this tetranuclear unit has been reported by Hubert-Pfalzgraf and co-workers with acetic acid [Nb$_4$O$_4$(Ac)$_4$(O^{i}Pr)$_8$][37] (Ac = acetate) or methacrylic acid [Nb$_4$O$_4$(MAA)$_4$(O^{i}Pr)$_8$][38] (MAA =

methacrylate) from niobium isopropoxide. For this series, starting niobium alkoxides plays a key-role in the synthesis of niobium(V) carboxylate complexes as the esterification process that is induced by the alkoxy groups (leaving as alcohol) and the carboxylic groups results in the production of water molecules and the creation of μ-oxo-bridges between niobium(V) atoms. A variant of these two configurations has been described by using bis(hydroxymethyl)propionic acid (H_2BHMP), in which two niobium-centered dimers containing one central μ-oxo groups are connected by both the carboxylate and hydroxy functions of the ligand[39]. This arrangement generates through the BHMP molecule, a tetranuclear species [(BHMP){Nb$_2$O(OEt)$_5$}$_2$], without any additional μ-oxo groups linking the niobium atoms. Another example of such an association of niobium carboxylate from the alkoxide route is also illustrated in a mixed bismuth-niobium moiety[40], which has been synthesized by means of salicylic acid (or 2-hydroxybenzoic acid) leading to a dinuclear [(Bi$_2$Nb$_2$O(OEt)$_2$(sal)$_4$(Hsal)$_4$)] or tetranuclear [(Bi$_2$Nb$_4$O$_4$(O^{i}Pr)$_4$(sal)$_4$(Hsal)$_3$)] (where sal = O$_2$C-C$_6$H$_4$-2-O; Hsal = O$_2$C-C$_6$H$_4$-2-OH) complexes. In both species, the presence of μ-oxo-bridges between niobium(V) atoms are observed. Considering the nuclearity aspect in molecular niobium carboxylates, the largest poly-oxo cluster was recently identified from the solvothermal reaction of niobium ethoxide with pivalic acid in an acetonitrile medium, which lead to the formation of the hexadecaniobate cluster [Nb$_{16}$O$_{28}$(OEt)$_{12}$(piv)$_{12}$][41].

Following our recent work on this topic, using aromatic monocarboxylic acid as ligands,[42] we decided to work with polytopic acids as ligands. Herein, we report on the investigation of the reactivity of polycarboxylic aromatic acids with niobium penta-ethoxide Nb(OEt)$_5$ precursor as the niobium(V) metal source. For this purpose, we have first used the tetratopic pyromellitic acid with Nb(OEt)$_5$ (compound **1**) followed by the use of larger polytopic ligands with an azobenzene core: the 4,4'-azobenzenedicarboxylic acid (compound **2**) and the 3,3',5,5'-azobenzenetetracarboxylic acid (compound **3**). Interestingly, the smallest ligand give rise to a mixture of niobium with different nuclearities while the bigger ones, with the azobenzene core, only lead to the stabilization of dinuclear {Nb$_2$O} moieties. These crystalline compounds were successfully characterized by single-crystal and powder X-ray diffraction and some insights in their formation behavior is given with the help of infrared and ^{1}H NMR spectroscopies.

Experimental Section

Reagents. The following reactants were used: niobium(V) ethoxide complex (Nb(OCH$_2$CH$_3$)$_5$, 99.95%, Sigma-Aldrich), pyromellitic acid (C$_{10}$H$_6$O$_8$, 96%, Sigma Aldrich), 4-nitrobenzoic acid (C$_7$H$_5$NO$_4$, 99%, Acros), D-(+)-glucose (C$_6$H$_{12}$O$_6$, 99.5%, Sigma Aldrich), sodium hydroxide (NaOH, 97%-100%, VWR). The chemical reactants were commercially available, were used without any further purification. The sensitive niobium(V) alkoxide precursor was used and manipulated in a glove box under argon to prevent any hydrolysis reaction of the niobium(V) alkoxide into niobium(V) oxide. The azobenzene carboxylic acid derivatives 4,4'-azobenzene dicarboxylic acid and 3,3',5,5'-azobenzene tetracarboxylic acid have been synthesized adapting a procedure described in literature.[43]

Syntheses

4,4'-azobenzene dicarboxylic acid. The organic linker (4,4'-azobenzenedicarboxylic acid, $C_{14}H_8N_2O_4$) was synthesized by modifying a protocol of the literature.[43] 4-nitrobenzoic acid (6.5 g, 36.0 mmol) and sodium hydroxide (25 g, 0.6 mol) were added in 120 mL H_2O and heated at 60 °C until dissolution. An aqueous solution of glucose (40 g in 75 mL of water) was heated up to 60 °C as well and then was added drop-wise to the previous solution. When the two solutions are mixed, the final solution is left to cool down for 30 minutes and then stirred for 16 hours under a strong air flow with vigorous stirring. The solution is then transferred to an ice bath and then filtered. The precipitate is dissolved in 125 mL of water and is acidified with the addition of drops of 37% HCl, precipitating an orange powder. The precipitate was filtered, washed and dried. (yield = 88 %).

3,3',5,5'-azobenzene tetracarboxylic acid. The organic linker (3,3',5,5'-azobenzenedicarboxylic acid, $C_{16}H_8N_2O_8$) was synthesized by modifying a protocol of the literature.[43] 5-nitroisophthalic acid (9.5 g, 44.9 mmol) and sodium hydroxide (25 g, 0.6 mol) were added in 120 mL H_2O and heated at 60 °C until dissolution. An aqueous solution of glucose (25 g in 50 mL water) was heated up to 60 °C as well and then was added drop-wise to the previous solution. When the two solutions are mixed, the final solution is left to cool down for 30 minutes and then stirred for 16 hours under a strong air flow with vigorous stirring. The solution is then transferred to an ice bath and then filtered. The precipitate is dissolved in 125 mL of water and is acidified with the addition of drops of 37% HCl, precipitating an orange powder. The precipitate was filtered, washed and dried. (yield = 82 %).

Compound 1 [(Nb$_2$(μ-O)(μ-OEt)(OEt)$_6$)$_2$(Nb(OEt)$_4$(HOEt))$_2$(C$_{10}$H$_2$O$_8$)]. A mixture of 0.75 mL (3 mmol) Nb(OCH$_2$CH$_3$)$_5$ and 76.2 mg (0.3 mmol) pyromellitic acid was placed in a 2 mL glass tube, sealed with a phenolic cap, and left at room temperature. Brick-like transparent crystals appeared after 3 months (Figure S1). Compound **1** was analyzed by optical and scanning electron microscope showing large block-shape crystals up to 50 µm size. The resulting colorless crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 10.8 %$_{Nb}$.

Compound 2 [(Nb$_2$(μ-O)(μ-OEt)(OEt)$_6$)$_2$(C$_{14}$H$_8$N$_2$O$_4$)]. A mixture of 0.5 mL (2 mmol) Nb(OCH$_2$CH$_3$)$_5$ and 8 mg (0.033 mmol) 4,4'-azobenzene dicarboxylic acid was placed in a 2 mL glass tube, sealed with a phenolic cap, and left at room temperature. Brick-like orange crystals appeared after 1 week (Figure S1). Compound **2** was analyzed by optical microscope showing parallelepiped-shape crystals up to 70 µm size. The resulting orange crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 12.8 %$_{Nb}$.

Compound 3 [(Nb$_2$(μ-O)(μ-OEt)(OEt)$_6$)$_4$(C$_{16}$H$_8$N$_2$O$_8$)]. A mixture of 0.5 mL (2 mmol) Nb(OCH$_2$CH$_3$)$_5$ and 10 mg (0.028 mmol) 3,3',5,5'-azobenzene tetracarboxylic acid was placed in a 2 mL glass tube, sealed with a phenolic cap, and left at room temperature. Plate-like yellowish crystals appeared after 4 weeks (Figure S1). Compound **3** was analyzed by optical

and microscope showing plate-shaped crystals up to 20 µm size. The resulting yellowish crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 7.3 %$_{Nb}$.

The purity of the compounds **1-3** was confirmed using powder X-ray diffraction analyses. Furthermore, no evidence of impurities was observed on the photographs of the three crystalline phases.

Single-crystal X-ray diffraction

Crystals of compounds **1**-**3** were selected under polarizing optical microscope and all crystals were mounted on MicroMount patented by MiTeGen, inserted into a goniometer base to perform single-crystal X-ray diffraction experiment. X-ray intensity data were collected on a Bruker DUO-APEX2 diffractometer using Mo-K_α radiation (λ = 0.71073 Å) with an optical fiber as collimator. Several sets of narrow data frames (20s per frame for **1** and **2** and 30s for **3**) were collected at different values of θ for two initial values of ϕ and ω, respectively, using 0.3° increments of ϕ with ω scans.

Data reduction was accomplished using SAINT V8.34a.[44] The substantial redundancy in data allowed a semi-empirical absorption correction (SADABS V2014/5) to be applied, on the basis of multiple measurements of equivalent reflections.[45] The structures were solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all F^2 data using SHELX program suites,[46] implemented in the OLEX2 graphical tool.[47]

The crystal data are given in Table 1. Supporting information is available in CIF format. CCDC numbers: 2179578 for **1**, 2179579 for **2** and 2179580 for **3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinements for compounds **1 - 3**.

	1	**2**	**3**
Formula	$C_{58}H_{122}Nb_6O_{34}$	$C_{42}H_{78}N_2Nb_4O_{20}$	$C_{72}H_{146}N_2Nb_8O_{40}$
Formula weight	1921.07	1302.7	2423.18
Temperature/K	107	100	100
Crystal type	colorless block	Orange block	Orange block
Crystal size/mm	0.85 x 0.52 x 0.45	0.24 x 0.24 x 0.12	0.132 x 0.098 x 0.083
Crystal system	monoclinic	monoclinic	triclinic
Space group	$C2/c$	$P2_1/n$	P-1
a/Å	24.0277(14)	15.3902(12)	8.0483(9)
b/Å	18.1923(11)	20.0542(14)	18.5558(19)
c/Å	19.0237(12)	17.5280(13)	18.624(2)
α/°	90	90	68.271(4)
β/°	97.308(3)	90.114(3)	81.253(5)
γ/°	90	90	84.084(5)
Volume/Å^3	8248.1(9)	5409.8(7)	2550.4(5)
Z, $\rho_{calculated}$/g.cm^{-3}	4, 1.547	4, 1.599	1, 1.578
μ/mm^{-1}	0.884	0.898	0.945
Θ range/°	1.71 - 26.42	1.32 - 26.41	1.339 – 26.428
Limiting indices	$-30 \leq h \leq 30$ $-22 \leq k \leq 22$ $-22 \leq l \leq 23$	$-19 \leq h \leq 19$ $-25 \leq k \leq 23$ $-21 \leq l \leq 21$	$-10 \leq h \leq 10$ $-22 \leq k \leq 23$ $-15 \leq l \leq 31$
Collected reflections	62529	78621	31082
Unique reflections	8239 [R(int) = 0.0350]	11078 [R(int) = 0.0479]	10333 [R(int) = 0.0999]
Parameters	612	660	655
Goodness-of-fit on F^2	1.050	1.022	1.010
Final R indices [I>2σ(I)]	R1 = 0.0580 wR2 = 0.1379	R1 = 0.0306 wR2 = 0.0715	R1 = 0.0675 wR2 = 0.1173
R indices (all data)	R1 = 0.0750 wR2 = 0.1521	R1 = 0.0357 wR2 = 0.0741	R1 = 0.1615 wR2 = 0.1442
Largest diff. peak and hole/e.Å^{-3}	2.28 and -1.18	0.95 and -0.82	0.74 and -1.27

Powder X-ray diffraction

X-ray powder diffraction was performed on Bruker D8 Advance diffractometer (LynxEye detector) in a Bragg-Brentano θ-θ mode using Cu-K$_\alpha$ radiation. Each powder pattern was recorded within an angular range of 5-50° in 2θ, with steps of 0.02° and counting time of 0.5 s per step.

NMR spectroscopy

The supernatants obtained after the crystallization of compounds **1** and **3** have been analyzed by solution ^{1}H-NMR at 300K and 9.4 T, on a Bruker Advance NEO 400 spectrometer equipped with a z-gradiented TBI 5 mm probe. In order to prevent any modification by adding any substance into the samples, the solution samples have been introduced in standard 5 mm tubes in which made inserted a coaxial insert (Eurisotop, Saint-Aubin, France) containing deuterated CDCl$_3$ (isotopic enrichment 99.8%, Eurisotop, Saint-Aubin, France) used for the lock and shims settings. Chemical shifts in parts per million (ppm) are referenced to the residual solvent peak of CHCl$_3$ at 7.26 ppm. Common abbreviations used in the NMR experiments are as follows: s singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m).

Scanning electron microscopy

The SEM analyses of niobium(IV) coordination complexes **1-3** were performed on a Hitachi-S3400N microscope, equipped with a tungsten filament (acceleration voltage = 15 kV, secondary electron mode, working distance = 5 to 10 mm).

IR spectroscopy

Infrared spectrum was measured on Perkin Elmer Spectrum Two[TM] spectrometer between 4000 and 400 cm^{-1}, equipped with a diamond Attenuated Total Reflectance (ATR) accessory. No ATR correction was applied on the spectrum.

Results and discussion

Structure Description

Compound 1 [(Nb$_2$(μ-O)(μ-OEt)(OEt)$_6$)$_2$(Nb(OEt)$_4$(HOEt))$_2$(C$_{10}$H$_2$O$_8$)] with C$_{10}$H$_2$O$_8$ = pyromellitate

The crystal structure of compound **1** displays an assembly of unusual centrosymmetric hexanuclear core centered around the pyromellitate ligand through niobium(V) connection with all its carboxylate arms (Figure 1). Two of them, located in an opposite side in 1,4-position, act as a bidentate bridging linker to two adjacent niobium atoms Nb1 and Nb2 with a *syn-syn* configuration. These two niobium centers are six-fold coordinated in a distorted octahedral geometry, to one μ-oxo (O6) group (Nb1-O6 = 1.940(3) Å; Nb2-O6 = 1.925(4) Å), one bridging μ-ethoxy group (Nb1-O5$_{Et}$ = 2.102(4) Å; Nb2-O5$_{Et}$ = 2. 147(4) Å) and three oxo groups from ethoxy molecules (Nb1-O$_{Et}$ in the range 1.876(3)-1.893(4) Å; Nb2-O$_{Et}$ in the range 1.865(4)-1.906(4) Å). The coordination sphere around the niobium atoms is completed by one oxygen atom (Nb1-O1$_c$ = 2.205(3) Å; Nb2-O7$_c$ = 2.206(3) Å) from the bidentate carboxylate group of the pyromellitate ligand. The occurrence of the μ-oxo groups does well agree with the BVS calculations (1.888 for O6).[48] It results in a dinuclear motif in which the two niobium-centered octahedral polyhedra are sharing edge through both μ-oxo and μ-ethoxy groups. The bidentate carboxylate pincer related to the Nb1⋯Nb2 axis, adopts a rotation of 90° compared to the benzene ring plane. Within this dinuclear sub-unit, the Nb1⋯Nb2 bond length is 3.2467(7) Å with an Nb1-O6-Nb2 angle of 114.3(2)°. These metric values are closely related to those of the

dinuclear niobium(V)-centered unit stabilized by only one carboxylate pincer, as it is observed in compounds **2** and **3**, with the azobenzene dicarboxylate and tetracarboxylate ligands.

The two other carboxylate groups (in 2,5-position) exhibit a monodentate connecting mode with a third niobium center. However, the situation is a bit more complicated since this niobium atom is delocalized on two close positions (Nb3A and Nb3B), offering a statistical disorder for the octahedral environment. Indeed, this niobium is six-fold coordinated to one oxygen atom from the carboxylate group and five oxygen atoms from ethoxy groups in terminal position, reflecting a mobility freedom for this set of atoms. The Nb3A-O12A$_c$ and Nb3B-O12B$_c$ bond distances are 2.149(11) and 2.148(11) Å, respectively. All the other Nb3-O$_{Et}$ bond lengths are ranging between 1.873(10) and 1.901(11) Å for Nb3A, and between 1.852(12) and 1.898(19) Å for Nb3B, as expected for the niobium attached to ethoxy group. However, it is observed that one of the Nb3-OEt distances of one ethoxy group exhibits a much longer unusual distance of 2.254(11) Å for sub-unit with Nb3A and 2.209(10) Å for sub-unit with Nb3B. Indeed, this oxo group (O15A or O15B) also interacts through hydrogen bonding with the free remaining oxygen atom from the carboxylate arm of the pyromellitate ligand (see dotted line in the Figure 1), as reflecting by the short O15A···O11A$_c$ and O15B···O11B$_c$ distances of 2.524(3) Å and 2.57(3) Å, respectively. The presence of ethanol molecule (instead of EtO$^-$) linked to the niobium Nb3 site is therefore considered for the fifth alkoxy ligand around Nb3. But due to disorder of the Nb3 site and the surrounding ethoxy/ethanol groups, it was not possible to clearly locate the hydrogen atoms of the EtOH species. The pyromellitate is fully deprotonated and acts as a hexadentate linker with six niobium atoms, four of them engaged in dinuclear moieties and two of them in mononuclear moieties. The resulting molecular species is neutral, due to the presence of one ethanol group attached to discrete sub-unit of niobium (Nb3), ensuring hydrogen bonding with the free carboxyl oxygen of the pyromellitate ligand. It is found that the orientation of this carboxylate group is nearly along the benzene ring plane. The occurrence of these two types of niobium sub-units (dinuclear and mononuclear in a *trans* configuration) is surely controlled by the steric hindrance of these motifs since relatively short methyl-methyl distances of 4.27(1) Å are observed between those from the dinuclear units and those from mononuclear units, preventing further niobium-oxo-niobium condensation in the mononuclear sub-unit. Anyway, it is an original condensation mode of the niobium ethoxy motifs through the polydentate ligand, 1,2,4,5-benzenetetracarboxylate, which has never been reported in literature up to now.

Such a connection mode with bridging μ_2-oxo, μ_2-ethoxy and carboxylate groups with two adjacent niobium atoms was previously reported in one complex stabilized by the bis(hydroxymethyl)propionate molecule.[39]
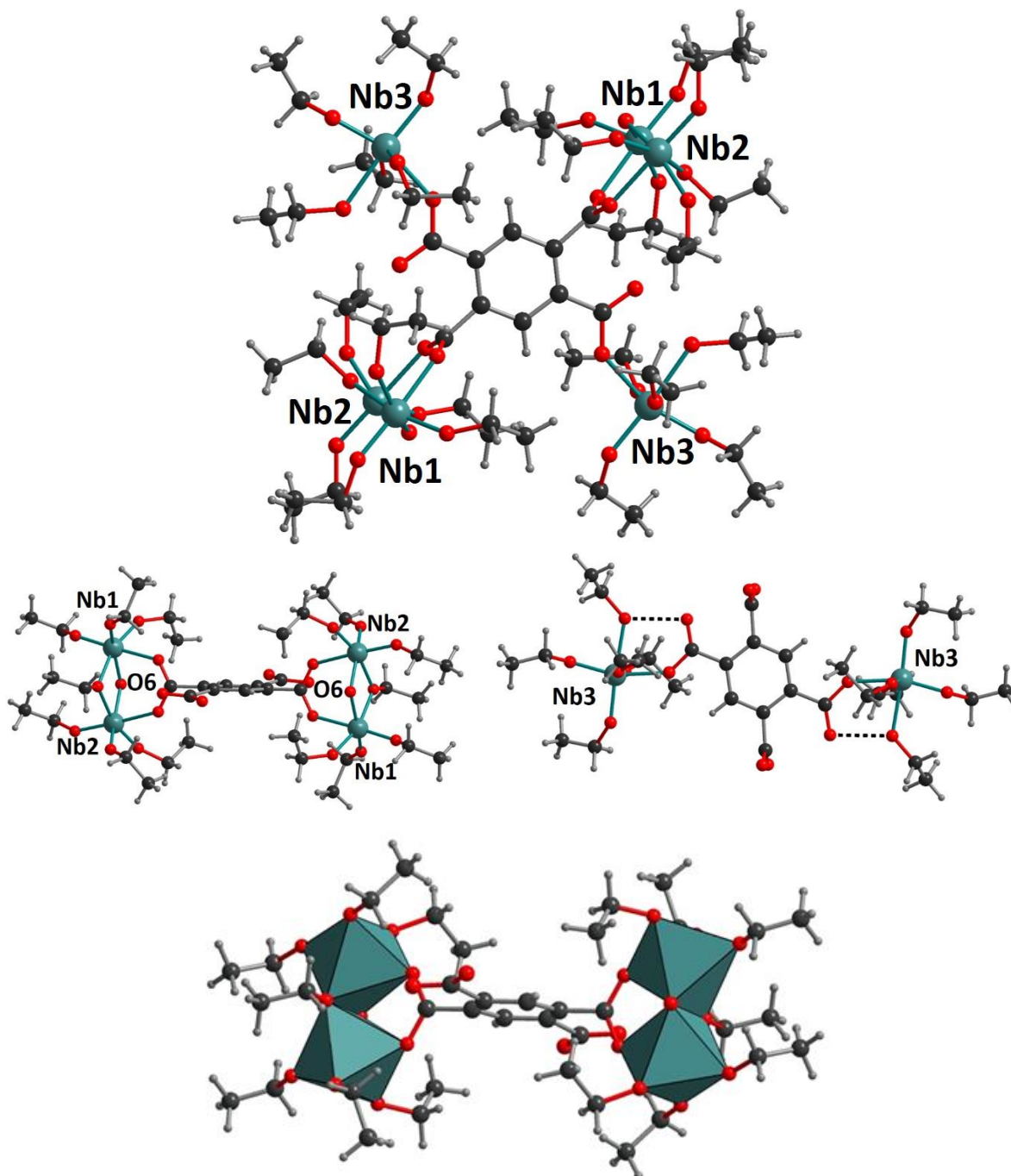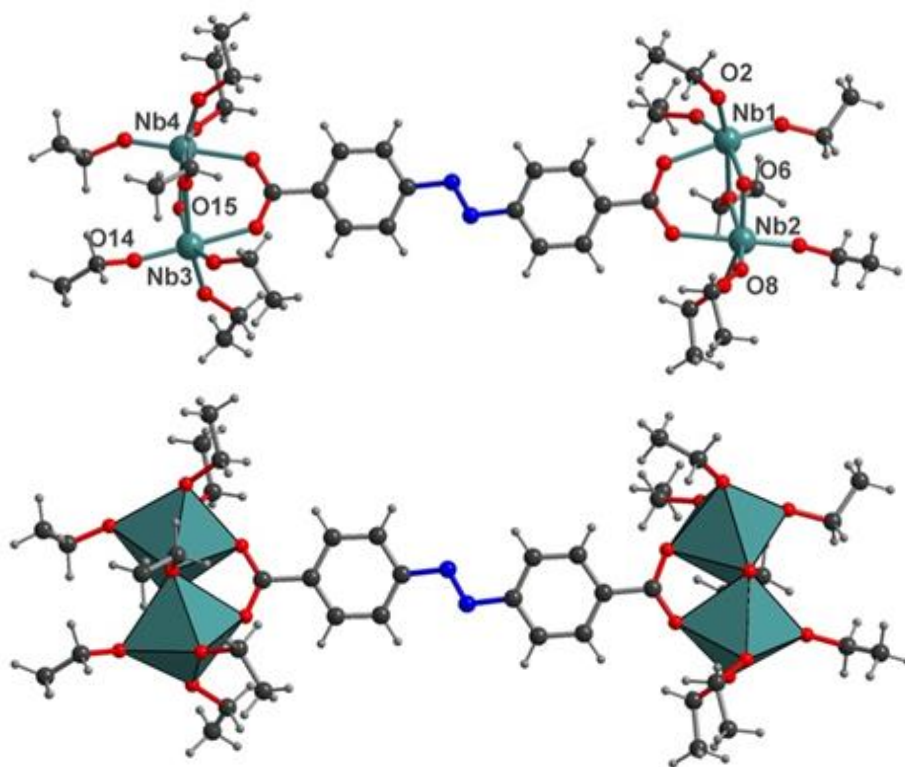
Figure 1. Ball and stick (top) and polyhedral (bottom) representations of the molecular hexanuclear coordination complex **1**. On left (top): view of the entire complex **1**; on right (top): detailed views of the connection mode of the carboxylate arm in 1,4 position and 2,5 position. One of the ethoxy groups linked to Nb1 site (through Nb1-O8 bonding) is disordered on two equivalent positions. Only one of these ethoxy groups is shown for clarity.

Compound 2 [(Nb$_2$(μ-O)(μ-OEt)(OEt)$_6$)$_2$(C$_{12}$H$_6$O$_4$)] with C$_{12}$H$_6$O$_4$ = 4,4'-azobenzene dicarboxylate

Compound **2** crystallizes in the monoclinic *P*2$_1$/*n* space group, with a structure displaying a molecular system composed of one 4,4'-azobenzenedicarboxylate ligand linking two niobium(V) dimers (Nb1-Nb2 and Nb3-Nb4) through the two bidentate carboxylate functions

(Figure 2). In this moiety, the four niobium(V) cations are six-fold coordinated with a distorted octahedral geometry. The environment is exclusively composed of oxygen atoms coming from one μ-bridging oxo (O6 for Nb1-Nb2 dimer and O15 for Nb3-Nb4 dimer) atom (Nb1-O6 = 1.930(2) Å; Nb2-O6 = 1.920(2) Å; Nb3-O15 = 1.926(2) Å and Nb4-O15 = 1.929(2) Å), one μ-bridging ethoxy group (Nb1-O5$_{Et}$ = 2.114(2) Å; Nb2-O5$_{Et}$ = 2.115(2) Å; Nb3-O16$_{Et}$ = 2.117(2) Å and Nb4-O16$_{Et}$ = 2.123(3) Å) and three terminal ethoxy molecules (Nb1-O$_{Et}$ in the range 1.865(2)-1.900(2) Å; Nb2-O$_{Et}$ in the range 1.849(2)-1.893(3) Å; Nb3-O$_{Et}$ in the range 1.866(2)-1.900(3) Å and Nb4-O$_{Et}$ in the range 1.863(3)-1.884(3) Å). The coordination sphere of each niobium centers is completed by one oxygen atom coming from the bidentate carboxylate functions of the azobenzene dicarboxylate ligand (Nb1-O1$_c$ = 2.188(2) Å; Nb2-O7$_c$ = 2.227(2) Å; Nb3-O11$_c$ = 2.191(2) Å and Nb4-O17$_c$ = 2.212(2) Å). In both dimers, the presence of the μ-oxo bridging atom is confirmed by BVS calculations (1.926 and 1.913 for O6 and O15 respectively).[48] Consequently, in the dimers, the two niobium centers share one edge through the binding of the bridging μ-oxo and μ-ethoxy groups. The bidentate carboxylate function related to the Nb1⋯Nb2 axis and Nb3⋯Nb4 axis, adopts a rotation of 20.868(83)° and 23.636(81)° respectively compared to the benzene ring plane. The two aromatic rings planes are slightly rotated with an angle of 3.106(98)°. In these two dinuclear sub-units, the Nb1⋯Nb2 and Nb3⋯Nb4 bond length is 3.2222(5) Å and 3.2412(5) Å with Nb1-O6-Nb2 and Nb3-O15-Nb4 angles of 113.64(12)° and 114.46(13)° respectively. The coordination modes of the niobium dimers is similar to the one described for the dimers in compound **1**.

Figure 2. Ball and stick (top) and polyhedral (bottom) representations of the molecular tetranuclear coordination complex **2**. The ethoxy groups linked to Nb1 site (through Nb1-O2 bonding), Nb2 site (through Nb2-O8 bonding) and Nb3 site (through Nb3-O14 bonding) are disordered on two equivalent positions. Only one of these ethoxy groups is shown for clarity.

Compound 3 [(Nb$_2$(μ-O)(μ-OEt)(OEt)$_6$)$_4$(C$_{16}$H$_8$N$_2$O$_8$)]: with C$_{16}$H$_8$N$_2$O$_8$ = 3,3',5,5'-azobenzene tetracarboxylate

Compound **3** crystallizes in the triclinic *P*-1 space group. The asymmetric unit of the crystal structure displays one half of the 3,3',5,5'-azobenzenetetracarboxylate ligand linking two distinct niobium(V) dimers (Nb1-Nb2 and Nb3-Nb4) through two bidentate carboxylate functions. The presence of an inversion center located between the two nitrogen atoms of the azo ligand generates the entire molecular complex, for which the ligand binds four niobium dimeric subunits (Figure 3). The composition of the dimers is similar to the one described for compounds **1** and **2.** All niobium(V) cations are six-fold coordinated with a distorted octahedral geometry, composed of oxygen atoms coming from one μ-bridging oxo (O1 for Nb1-Nb2 dimer and O11 for Nb3-Nb4 dimer) atom (Nb1-O1 = 1.913(4) Å; Nb2-O1 = 1.944(4) Å; Nb3-O11 = 1.930(6) Å and Nb4-O11 = 1.933(5) Å), one μ-bridging ethoxy group (Nb1-O7$_{Et}$ = 2.111(4) Å; Nb2-O7$_{Et}$ = 2.124(4) Å; Nb3-O17$_{Et}$ = 2.124(6) Å and Nb4-O17$_{Et}$ = 2.121(6) Å) and three terminal ethoxy molecules (Nb1-O$_{Et}$ in the range 1.855(5)-1.907(4) Å; Nb2-O$_{Et}$ in the range 1.858(5)-1.894(5) Å; Nb3-O$_{Et}$ in the range 1.865(6)-1.883(5) Å and Nb4-O$_{Et}$ in the range 1.846(5)-1.904(6) Å). The coordination sphere of each niobium centers is completed by one oxygen atom coming from the bidentate carboxylate functions of the azobenzene dicarboxylate ligand (Nb1-O3$_c$ = 2.202(4) Å; Nb2-O2$_c$ = 2.234(4) Å; Nb3-O12$_c$ = 2.234(4) Å and Nb4-O13$_c$ = 2.188(4) Å). In both crystallographically independent dimers, the presence of one μ-oxo bridging atom is confirmed by BVS calculations (1.909 and 1.892 for O1 and O11 respectively).[48] Alike the other niobium dimers in compounds **1** and **2**, the two niobium centers share one edge through the binding of the bridging μ-oxo and μ-ethoxy groups. The bidentate carboxylate function related to the Nb1$\cdots$Nb2 axis and Nb3$\cdots$Nb4 axis, adopts a rotation of 9.797(152)° and 7.398(193)° respectively compared to the benzene ring plane. The two aromatic rings planes perfectly coplanar and no deviation angle is measurable. In these two dinuclear sub-units, the Nb1$\cdots$Nb2 and Nb3$\cdots$Nb4 bond length is 3.2322(9) Å and 3.2184(12) Å with Nb1-O1-Nb2 and Nb3-O11-Nb4 angles of 113.9(2)° and 112.8(3)° respectively. The coordination modes of the niobium dimers generating {Nb$_2$O} sub-groups, are identical to the one described for the dimers in compounds **1** and **2**.
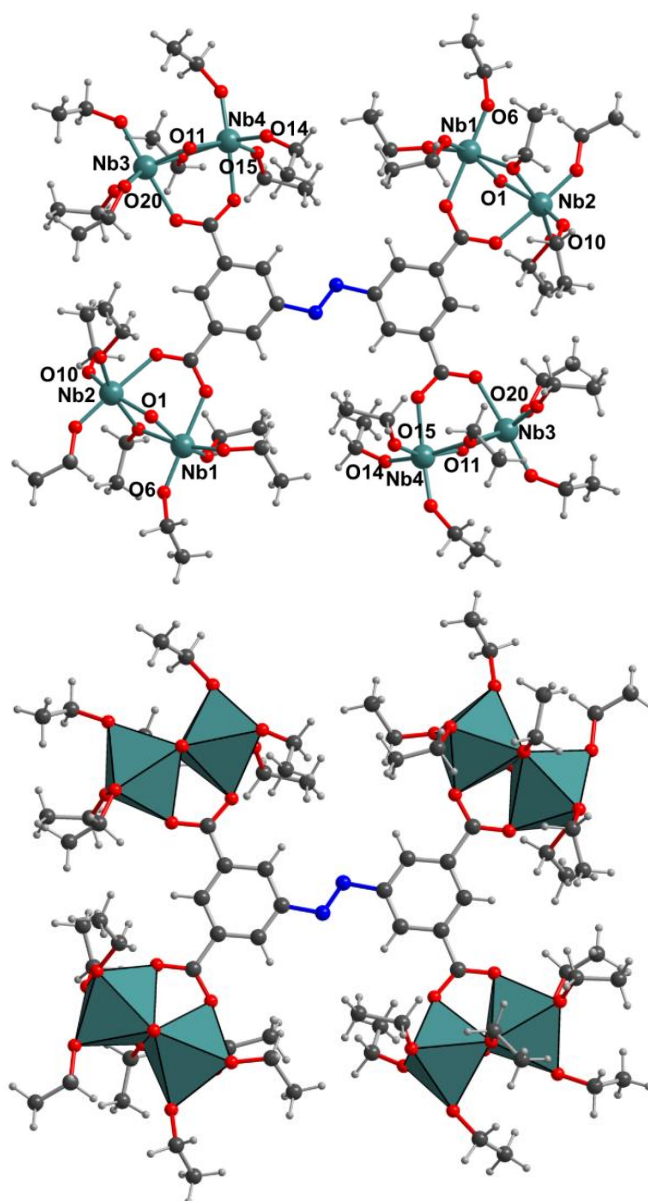
Figure 3. Ball and stick (left) and polyhedral (right) representations of the molecular octanuclear coordination complex **3**. The ethoxy groups linked to Nb1 site (through Nb1-O6 bonding), Nb2 site (through Nb2-O10 bonding), Nb3 site (through Nb3-O20 bonding) and Nb4 site (through Nb4-O14 and Nb4-O15 bondings) are disordered on two equivalent positions. Only one of these ethoxy groups is shown for clarity.

**Crystal packing and intramolecular interactions**

The three described systems are completely solvent free. Consequently, the interactions stabilizing such spatial arrangement can only come from the aromatic and aliphatic sub-groups of the compounds. A close look on the three systems reveals the presence of numerous CH-π interactions taking place between hydrogen atoms of the CH$_3$ groups of some ethoxide ligands and the aromatic rings of the central ligands. The $C_H \cdots C_{Ar}$ interaction distances lie in the range 3.1268(37)-3.8726 Å, 3.0208(31)-3.5065(31) Å and 2.7572(70)-3.8482(66) Å for compound **1**, **2** and **3** respectively. The packing of the three compounds (Figure S2a, S2b and S2c) shows no classic π-π interactions in compounds **2** and **3** despite the apparent stacking when looking along the *a* axis. This is due to the steric hindrance generated by the niobium centers, causing the

aromatic rings to be distant of 7.4072(44) Å to 7.5572(44) Å and 8.0483(105) Å in compounds **2** and **3** respectively. In compound **1**, the layers of molecules adopt a A-B-A-B organization visible through the 110 direction as shown on Figure S2a.

Infrared spectroscopy

The three different niobium(V) ethoxide – carboxylic acid systems in compounds **1**-**3**, were investigated by using infrared spectroscopy, in order to characterize their crystallization process. For each batch, the supernatant solutions have been studied just after the starting reactants mixing at t = 1h at room temperature, and then after the crystallization of the compounds (3-months, 1-week and 1-month duration for compounds **1**, **2** and **3**, respectively). On the spectrum, several zones are of interest and can be attributed to the ethoxide ligands.[49] Indeed, the 3050-2750 cm^{-1} range is related to the ν(C-H) stretching vibrations of the ethyl groups (with typical bands at approximately $2970_{(asym)}$ and $2860_{(sym)}$ cm^{-1}) and, the 1480-1370 cm^{-1} zone is related to the ν(C-H) bending vibrations of the methyl groups (with typical bands in the range 1470-1404 and around 1375 cm^{-1}). The bands about 1200-1000 cm^{-1} are assigned to the ν(C-O) vibrations coming from the ethoxide group linked to niobium center through Nb-O-C$_{Et}$ linkage. Typical peaks are found at 1100-1090 cm^{-1} and 1060-1040 cm^{-1}. The broad peaks centered at 529-522 cm^{-1} are related to ν(Nb-O) stretching modes.[50] These different signatures are observed in the niobium precursor, the supernatant solutions and crystallized niobium complexes, as expected.

For our interest in the formation of niobium carboxylate complexes, we focused our attention on the 1750-1550 cm^{-1} region, where free carboxylic acid ν(C=O), and bonded carboxylate ν_{asym}(COO) and ν_{sym}(COO) stretching vibrations are typically found. For complexes **1**-**3**, we observed the same trends (Figures 4, S4a and S4b), since unprotonated carboxylate ligands are always visible in the supernatant solutions after mixing the chemical reactants (see Table 2). Indeed, for compound **1** system, the band at 1698 cm^{-1}, is related to the ν(C=O) stretching from pyromellitic acid, but disappears when it is mixed with the niobium ethoxide solution. The corresponding vibration stretching is shifted to 1598 cm^{-1} and 1541 cm^{-1} and is attributed to the ν_{asym}(COO) and ν_{sym}(COO), respectively. It reveals the bonding between the carboxylate group of the ligand and the niobium centers[51] in supernatant solution, just after 1h mixing. This observation indicates the relatively rapid complexation of the starting niobium ethoxide by the carboxylate group occurring at room temperature in less than an hour, and therefore the presence of niobium-ethoxide-carboxylate in solution. It also highlights the fact that the acid form of the ligand solubility is relatively weak as it is not observed on the supernatant before crystallization. Interestingly, a new vibration band appears at 1729 cm^{-1} in both the supernatant after one month and the crystalline phase (Figure 4). It is assigned to the ν(C=O) coming from the formation of an ethyl-pyromellitate ester. Such formation was previously reported on the synthesis of a tetranuclear niobium acetate[51] or aryl-carboxylates[42] compounds and is expected to come from the reaction of the acid with the ethoxide groups (forming ethyl-ester and water) coming from the niobium precursor. As a result, it indicates the complexation of the carboxylic ligand to the niobium centers releasing some of the ethoxy molecules allowing the esterification reaction.
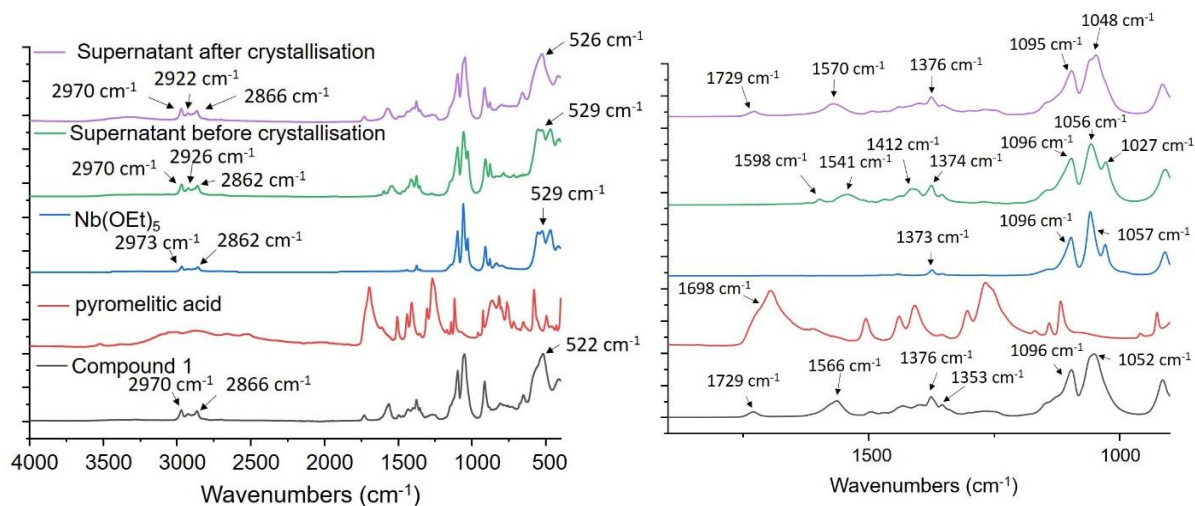
Figure 4. Infrared spectroscopy analysis for the niobium(V) / pyromellitic acid system **1**. Nb(OEt)$_5$ (blue line), pyromellitic acid (red line), supernatant solution after 1h mixing at room temperature (green), supernatant after crystallization for 3 months at room temperature (purple) and compound **1** (black line). left: full spectrum in the 4000-400 cm^{-1} range; right: detailed region in the 1900-950 cm^{-1} range.

The reactivity of the carboxylic acid toward the niobium ethoxide described above is also observed for the different crystallization processes of compounds **2** and **3**. The ν(C=O) stretching from 4,4'azobenzenedicarboxylic acid and 3,3',5,5'azobenzenetetracarboxylic acid is observed at 1681 cm^{-1} and 1685 cm^{-1} respectively but, is not observed as it is in the supernatant, indicating again the low solubility of the acid form of the ligands in the niobium precursor. The two ligands ν(C=O) stretching vibrations both disappear when the ligand is mixed with the niobium ethoxide solution to give the corresponding vibration at 1591 cm^{-1} in addition to those at 1543 cm^{-1} and 1605 cm^{-1} plus 1559 cm^{-1}, related to the ν$_{asym}$(COO) and ν$_{sym}$(COO), for crystals of compound **2** and **3**, respectively. However, the infrared signatures differ from what could be expected for both supernatant solutions before and after crystallization. Indeed, before crystallization, the ν(COO) vibrations bands are present but appear extremely weak, indicating that the niobium carboxylate compounds are present in solution at a very low concentration. Consequently, the "soluble" niobium-ethoxide-carboxylate complex is probably quickly transformed into the solid crystalline form. ^{1}H NMR spectra of the supernatant after 1 hour confirm this suggestion as the signals corresponding to the ligand are extremely weak. In addition, for compound **3**, these ν(COO) vibrations are not visible on the IR spectra indicating that the system has crystallized and is not present in the supernatant anymore.

Table 2. Comparison of the ν(C=O) vibrations (from carboxylic acid function) and ν(COO) vibrations (from carboxylate function) for the complexes **1**-**3** (in cm^{-1}).

		ν(C=O)$_{acid}$	ν$_{asym}$(COO)	ν$_{sym}$(COO)
Compound 1	pyromellitic acid	1698	/	/
	supernatant (1 hour)	/	1598	1541
	supernatant (1 month)	/	n.o.[a]	1570
	crystalline product	/	n.o.[a]	1566

Compound 2	4,4'-azobenzene dicarboxylic acid	1681	/	/
	supernatant (1 hour)	/	1597	1541
	supernatant (1 month)	/	1597	/1551
	crystalline product	/	1591	1543
Compound 3	3,3',5,5'-azobenzene tetracarboxylic acid	1685	/	/
	supernatant (1 hour)	/	1598	1538
	supernatant (1 month)	/	n.o.[a]	n.o.[a]
	crystalline product	/	1605	1559

[a]n.o. : not observed.

Solution NMR spectroscopy

The crystallization process of the three systems was also investigated using solution ^{1}H NMR and ^{13}C-^{1}H HMBC correlations. We have analyzed the supernatant solutions before and after crystallization occurs. For system **2** and **3**, no informations regarding the state of the ligands (acid form, ester form or complexed form) were obtained despite our efforts. In contrast, the measurements performed on system **1** (with the pyromellitic ligand) give some insight on the crystallization process, based on the signals present in the aromatic region of the spectra. In system **1**, the aromatic region of the spectrum in the supernatant after one hour already shows the presence of several extremely weak peaks distributed over two main signals centred at 7.77 ppm and 7.70 ppm (Figure S5a top). It suggests that the ligand already react with some ethanol molecules coming from the niobium precursor to form ethyl esters derivatives as the acid form of the ligand should only give one signal. After one month, the ^{1}H supernatant spectrum shows the presence of numerous peaks, two of them being related to an ester form of the ligand as shown by the ^{1}H-^{13}C HMBC correlation (Figure S5a bottom and S5b). The other signals may be related to complex form of the ligand or to ligands with partial esterification of the four carboxylic functions.

Discussion

The reaction of the aromatic polycarboxylic ligands with the niobium(V) ethoxide precursor lead to the formation of three crystalline molecular compounds containing a number of niobium centers going from four to eight which is comparable from this aspect to most of the complex obtained with various monotopic ligands in literature or very recently, in our group.[42] In addition to the carboxylate complexation, the common feature is the occurrence of one μ-oxo groups bridging two adjacent niobium centers in all dimeric {Nb$_2$O} units. The generation of this bridging oxygen atoms is due to the reaction between the carboxylic acid ligands and leaving ethoxide groups from the niobium {Nb(OEt)$_5$} precursor generating a small quantity of water (by-product of the esterification reaction) thus allowing the following condensation reaction forming the niobium dimer : $2 \times Nb(OEt)_5 + H_2O \rightarrow Nb\text{-}O\text{-}Nb + 2 \times EtOH$.

The crystalline phase obtained in the three systems was confirmed to be pure by powder X-ray diffraction analysis (Figure S3a, S3b and S3c). The main point of differentiation lies in the arrangement of the molecular systems. Indeed, in the case of monotopic ligand, the coordination

complexes are systematically constructed around the polynuclear niobium clusters with the organic ligands surrounding it whereas, in compounds **1-3**, the ligand plays the central role with the niobium moieties surrounding it. This observation is obviously logical but could explain the difficulty to grow niobium clusters with high nuclearities when using polycarboxylate ligands. In this view, a similar arrangement was reported for a reduced niobium(IV) form complex, stabilized by ditopic (terephthalic or isophthalic acid) or tritopic (trimesic acid) aromatic linker, with the series of $[(Cp'_2Nb)_{2 or 3}(ligand)]$ where Cp' is a cyclopentadienyl species of type η^5-$C_5H_4SiMe_3$. In the latter, the central di- or tritopic carboxylate ligand connects two or three niobium(IV) center, via chelating connection modes of each carboxylate arms.[52]

The coordination modes of the carboxylate function differ within compound **1** in comparison with compounds **2** and **3**. In the latter, each arm of the carboxylate ligands appears well spaced and, are engaged, in a bidentate bridging mode, to two and four dimeric niobium $Nb_2(\mu-O)(\mu-OEt)$ moieties. No particular steric hindrance due to the ethoxy groups is observed around the niobium centers and, the binding functions form relatively flat coordination angles in both compounds, ranging from 7.398(193)° to 23.636(81)°. On the opposite, in compound **1**, the four carboxylate groups of the pyromellitate ligand are relatively close causing a drastic change in these coordination modes due to the steric hindrance generated by the ethoxy ligands. Consequently, the two carboxylate functions adapt their coordination and adopt a 90° rotation angle compared to the benzene ring. In addition, the two other carboxylate functions located in adjacent position on the benzene ring appear unable to bind a niobium dimer and only one niobium centre is complexed in a monodentate way.

The studies of the formation behaviour of complexes **1-3** by IR and ^{1}H NMR is difficult to exploit because of the very low solubility of the polycarboxylic ligands in the niobium(V) ethoxide precursor as it can be seen on the ^{1}H NMR spectrum of supernatant solution of system **1**. For system **2** and **3**, no signals corresponding to the ligand were clearly observed and informations were obtained only for system **1**. Indeed, two weak groups of peaks in the aromatic region, centred at 7.77 ppm and 7.70 ppm are observed on the spectrum of the supernatant before crystallization. Their presence suggests the reaction of the ligand with ethanol molecules coming from the niobium precursor to form ethyl esters derivatives as the acid form of the ligand should only give one signal. This is indirectly confirmed by the IR spectroscopy of the supernatant where we can see the appearance of $\nu_{sym}(COO)$ and $\nu_{asym}(COO)$ corresponding to the carboxylate form of the ligand complexed to the niobium cations. The released ethoxy groups from the precursor are then able to undergo an esterification reaction with the free acid pyromellitic ligand. After the crystallization process occurs, the supernatant spectrum shows the presence of numerous peaks (Figures S5a bottom). ^{13}C-^{1}H HMBC correlation on these signals shows that two of them located at 8.73 ppm and 8.62 ppm seems to be related to an ester form (Figure S5a top and S5b). This fact is further reinforced by the IR spectrum of the same solution where the presence of ester could be detected (band located at 1729 cm^{-1}, Figure 4). IR spectra of supernatant solutions of systems **2** and **3** before crystallisation confirm the almost insolubility of the organic ligand. We can only see very weak $\nu_{sym}(COO)$ and $\nu_{asym}(COO)$ vibrations bands at ~1540 cm^{-1} and ~1600 cm^{-1} respectively (Figure S3a and S3b) indicating that coordination took place with the niobium precursor. No such information is visible on the supernatant after crystallisation for compound **3** but the solid crystalline material presents the same $\nu_{sym}(COO)$ and $\nu_{asym}(COO)$ vibrations (Figure S4a and S4b). Nevertheless, for all three

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compounds, these observations confirm the complexation of the carboxylate functions of the polytopic organic linkers to the niobium centres as described in the structural analysis section.

Conclusion

The use of tetracarboxylic acid ligands successfully leads to the formation of three new molecular compounds with niobium monomers or {Nb$_2$O} dinuclear oxo-clusters. The presence of these dinuclear moieties containing an oxo bridge are made possible due to the synthetic conditions. The leaving ethanol molecules from the niobium ethoxide precursor react with the acid precursor to form ester and water, allowing the condensation process. From structural point of view, all three compounds possess dinuclear entities but, only the one constructed using the pyromellitate ligand is assembled from a mixture of monomeric and dimeric niobium groups. This ligand is smaller than the 3,3',5,5'-azobenzene tetracarboxylate also used in this work and consequently, it probably does not leave enough room for the presence of four dinuclear clusters. We are currently working on other polycarboxylate ligands to attempt the formation of extended coordination networks.

Conflict of interests

The authors declare no conflict of interests.

Associated Content

Supporting Information for this article is available on the WWW under https://doi.org/10.1039/D2CE00XXX.

The data associated with the findings of this study can be found in the online version (optical microscope photographs, powder XRD pattern, IR spectra, liquid ^{1}H NMR and solid state ^{93}Nb spectra).

Accession Codes

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 2179578 for **1**, 2179579 for **2**, 2179580 for **3**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336-033; e-mail: data_request@ccdc.cam.ac.uk).

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