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Structural variety of niobium(V) polyoxo clusters obtained from the reaction with aromatic monocarboxylic acids: isolation of $\{Nb_2O\}$, $\{Nb_4O_4\}$ and $\{Nb_8O_{12}\}$ cores

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Table of Content (TOC) Graphic

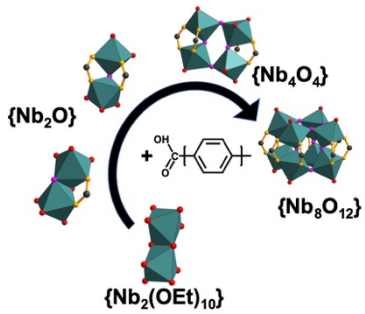


Table of Content (TOC) Synopsis

Polynuclear niobium(V)-based carboxylate oxo clusters: a series of aryl monocarboxylate ligands is used for the isolation of molecular coordination complexes corresponding to dinuclear $\{Nb_2O\}$, tetranuclear $\{Nb_4O_4\}$ or octanuclear $\{Nb_8O_{12}\}$ niobium(V)-centered poly-oxo clusters related to different hydrolysis rate.

ABSTRACT: The reactivity of aryl monocarboxylic acids (benzoic, 1- or 2-naphtoic, 4'-methylbiphenyl-4-carboxylic and anthracene-9-carboxylic acids) has been investigated as complexing agent toward the ethoxide niobium(V) ($Nb(OEt)_5$ precursor. A total of 8 coordination complexes has been isolated with distinct niobium(V) nuclearities as well as carboxylates complexation states. The use of benzoic acid gives to a tetranuclear core $Nb_4(\mu_2\text{-}O)_4(L)_4(OEt)_8]$ (*L* = benzoate (**1**)) exhibiting four Nb-(μ_2-O)-Nb linkages in a square plane configuration. A similar tetramer (**7**) is obtained with 2-naphtoic acid by using a 55% humidity atmosphere synthetic route. Two types of dinuclear bricks has been identified with one central Nb-(μ_2-O)-Nb linkages, and differ by the complexation state, with one bridging carboxylate ($[Nb_2(\mu_2\text{-}O)(\mu_2\text{-}OEt)(L)(OEt)_6]$, with *L* = 1-naphtoate (**3)** & *L* = anthracene-9-carboxylate (**5**)) or two bridging carboxylate groups ($[Nb_2(\mu_2\text{-}O)(L)_2(OEt)_6]$, with *L* = 4'-methylbiphenyl-4-carboxylic (**4)** & *L* = anthracene-9-carboxylate (**6**)). An octanuclear moiety $[Nb_8(\mu_2\text{-}O)_{12}(L)_8(\eta_1\text{-}L)_{4-x}(OEt)_{4+x}]$ (with *L* = 2-naphtoate, x = 0 or 2; **8**) has been obtained by using solvothermal route in acetonitrile, and possesses a cubic configuration with niobium centers at each node, linked through 12 μ_2-O groups. The formation of the niobium oxo clusters has been characterized by infrared and liquid ^{1}H NMR spectroscopy in order to analyze the esterification reaction, which induce the release of water molecule, which further reacts through oxolation process with niobium atoms, in different $\{Nb_2O\}$, $\{Nb_4O_4\}$ and $\{Nb_8O_{12}\}$ nuclearities.

Introduction

The remarkable development of the porous Metal-Organic Framework (MOF) materials has drastically renewed the chemistry of metal carboxylates, since most of these crystalline solids are built up from the basic assemblies consisting of inorganic cores linked to each other through organic ligand via M-O-C bondings. Indeed, the chemical richness of such associations lies on the library of the large number of various polytopic organic molecules, but a rather limited choice of metallic elements, related to their availability to produce stable metal carboxylate linkages for generating three-dimensional open frameworks. The majority of MOF compounds involves the use 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), but a few solids are related to higher valence cations[1]. We may quote the quite unique case encountered for the uranyl chemistry related to the oxidation state +6 for uranium. But due to its specific configuration of double trans oxo ligands, this 5*d* element rather behaves as a formal divalent cationic species corresponding to the UO_2^{2+} moiety, giving rise to a myriad of organic-inorganic networks when associated with organic linkers, as we observed for other divalent transition metals[2]. In fact, the reactivity of the high valence transition metals with carboxylic acids has been hardly investigated, despite the occurrence of some coordination complexes involving carboxylate ligands.

Among the candidates with high valence cations, niobium(V) has drawn our attention because its chemistry was reported in very rare cases related to the context of the elaboration of MOF materials. Thus, some recent works described the incorporation of niobium as a doping element, into various MOF well-known 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 aim to study properties in catalysis field or modification in electronic structures. To our knowledge, the synthesis of niobium-based MOF structures has not been explored with carboxylate species as organic linkers. However, niobium has been encountered in MOF-like compounds as an oxyfluorinated $(NbOF_5)^{2-}$ basic building brick in a mixed Nb-Ni square network (KAUST-7) with pyrazine ligands[7] or as mononuclear Nb-node in a layered honeycomb lattice with 3,6-dichloro 2,5-dihydroxybenzoquinone ligand[8].

If extended networks are not considered, there nevertheless exist several coordination complexes of niobium stabilized by carboxylate molecules in molecular assemblies. It can be found as a commercial precursor in a discrete Nb-centered mononuclear unit, when precipitated by oxalic acid to give either identified $[A][NbO(C_2O_4)_2(H_2O)_2]\cdot xH_2O$ (A = NH_4^+[9],[10] or Cs^+ [11]) or $[A]_3[NbO(C_2O_4)_3]\cdot xH_2O$ (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 are been identified in the presence of barium in $[Ba_2(H_2O)_5][NbO(C_2O_4)_3][HC_2O_4]\cdot H_2O$[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 coordination complexes have been isolated starting from niobium pentachloride or niobium alkoxides precursors.

For the first family, the reactivity of benzoic acid (HO_2C-C_6H_5) has been tested with the halide precursor, which gave rise to the formation of molecular dinuclear complexes, in which the niobium centers are bridged through the carboxylate arm of the monotopic benzoate molecules. In one case, the dimer $[Nb_2Cl_6(O_2C$-$C_6H_5)_2O]$[23] also showed additional μ_2-oxo group linking the two adjacent niobium centers, whereas it does not exist in a second dimer $[Nb_2Cl_4(OEt)_4(O_2C$-$C_6H_5)_2]$[24]. Other benzoate derivatives (O_2C-R where R = FC_6H_4, *p*-ClC_6H_4, *p*-IC_6H_4, *p*-MeC_6H_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_2-oxo group. A related dinuclear complex has also been identified with fluorosubstituted benzoate linker (O_2C-C_6F_5) for the purely chloride salt $[Nb_2Cl_8(O_2C$-$C_6F_5)_2]$[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 metallo-organic 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 attribute to the alteration and modification of its properties [31],[32],[33],[34],[35],[36]. Regarding the chemistry of niobium alkoxides, many coordination 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 $[Nb_2O(O_{Nep})_6(piv)_2]$ (where O_{Nep} = OCH_2CMe_3 or Neopentanoxy) in the presence of pivalic acid (Me_3C-CO_2H = *H*piv). Its structure is related to the dimer $[Nb_2Cl_6(O_2C$-$C_6H_5)_2O]$[26] obtained from the halide route, with two carboxylate arms from pivalate ligand and one bridging μ_2-oxo group. Here, the chloro anions are substituted by the neopentanoxy groups. However, in the same system, when using the terbutylacetic acid (Me_3C-CH_2-CO_2H = *H*tBAc), a higher condensed coordination complex has been isolated with four niobium centers placed in a square configuration, and connected to four μ_2-oxo groups $[Nb_4O_4(O_{Nep})_8(tBAc)_4]$. This dimeric moiety can be seen as the association of the two previously described dinuclear bricks $[Nb_2O(O_{alkoxide})_3(carboxylate)_2]$ linked to other by two additional μ_2-oxo groups. Indeed, this tetranuclear unit has been reported by Hubert-Pfalzgraf and co-workers with acetic acid $[Nb_4O_4(Ac)_4(O^iPr)_8]$[37] (ac = acetate) or methacrylic acid $[Nb_4O_4(MAA)_4(O^iPr)_8]$[38] (MAA = methacrylate) from niobium isopropoxide. For this series, starting niobium alkoxides plays a key-role in the synthesis of niobium(V) carboxylate coordination 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_2-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_2-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 $[(BHMP)\{Nb_2O(OEt)_5\}_2]$, without any additional μ_2-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 $[(Bi_2Nb_2O(OEt)_2(sal)_4(Hsal)_4)]$ or tetranuclear $[(Bi_2Nb_4O_4(O^iPr)_4(sal)_4(Hsal)_3)]$ (where sal = O_2C-C_6H_4-2-O; *H*sal = O_2C-C_6H_4-2-OH) coordination complexes. In both species, the presence of μ_2-oxo-bridges between niobium(V) atoms are observed. Related to the nuclearity 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 yielded to the formation of the species $[Nb_{16}O_{28}(OEt)_{12}(piv)_{12}]$[41].

In this contribution, our work deals with the investigation of the reactivity of aromatic monocarboxylic acid, by using the alkoxide route from niobium penta-ethoxide ($Nb(OEt)_5$) as metallic precursor. Indeed, this synthetic pathway was previously reported with $NbCl_5$ combined to derivatives of benzoic acids[23],[24],[42]. Therefore, the first study was focused on the reaction of benzoic acid with $Nb(OEt)_5$ (compound **1**), then followed by the reaction of other aromatic carboxylic acids such as 2-naphthoic acid (compounds **2**, **7** & **8**), 1-naphthoic acid (compound **3**), 4'-methylbiphenyl-4-carboxylic acid (compound **4**) and anthracene-9-carboxylic acid (compounds **5** & **6**). By changing the nature of ligands and synthetic conditions, a total of eight coordination complexes have been isolated with nuclearities varying from 2 $\{Nb_2O\}$ up to 4 $\{Nb_4O_4\}$ and 8 $\{Nb_8O_{12}\}$. An understanding of condensation mechanisms is proposed and based on infrared and ^{1}H liquid-state NMR, ^{1}H-^{13}C HMBC 2D correlation spectroscopies, in order to examine the esterification reaction occurring during the crystal growth of such compounds.

Results and discussion

Structure Description

Compound $[Nb_4(\mu_2\text{-}O)_4(C_7H_5O_2)_4(OEt)_8]$ (1)

The crystal structure of compound **1** is described from a centrosymmetric molecular tetranuclear core (Figure 1) bearing two crystallographically independent niobium atoms, Nb1 & Nb2. Both cationic centers are six-fold coordinated with two μ_2-oxo groups (Nb1-O3 = 1.913(3) Å; Nb1-O4 = 1.899(3) Å; Nb2-O3 = 1.918(3); Nb2-O4 = 1.885(3) Å), two carboxyl oxygen atoms from benzoate ligands (Nb1-O_c = 2.172(3)-2.176(3) Å; Nb2-O_c = 2.154(3)-2.178(3)Å) and two oxygen atoms from ethoxy groups (N1-O_{Et} = 1.833(4)-1.888(3) Å; Nb2-O_{Et} = 1.850(4)-1.883(3) Å). The presence of the bridging μ_2-oxo group agrees well with bond valence calculations 1.976 for O3; 2.106 for O4)[43]. The μ_2-oxo groups are bridging two adjacent niobium atoms and are located in *cis* position in the $\{NbO_6\}$ octahedra, resulting in a square ring of Nb1-O-Nb2 bondings within the tetrameric brick. The Nb1···Nb2 bond lengths are in the range 3.649(5)-3.664(4) Å, with Nb-O-Nb angles of 146.0(2)° (concave bending of Nb1-O3-Nb2 bond) and 149.3(2)° (convex bending of Nb1-O4-Nb2 bond). For one Nb1-O3-Nb2 sub-unit, the carboxylate arms from the benzoate molecule occupy a *cis* position, leading to one benzene group located along the Nb1-O3-Nb2 square plane, and a second benzene group placed either up or down perpendicularly to Nb1-O3-Nb2 square plane. The carboxylate group adopts a *syn-syn* bidentate bridging fashion with two neighboring niobium centers Nb1 and Nb2, linked through the μ_2-O3 groups only. The neutral tetranuclear core is decorated by ethoxy

groups attached to the niobium atoms. One of them (O8) linked to Nb1, is found to be disordered on two crystallographic positions. This tetrameric building block $\{Nb_4O_4\}$ can be seen as the association of two dinuclear sub-unit of type $[Nb_2(\mu_2\text{-}O)(C_7H_5O_2)_2(OEt)_6]$, closely structurally related to that of coordination complexes **2-3** (see hereafter) for which two sets of two ethoxy groups has been formally substituted by one additional μ_2-oxo group (here O4) in order the generate the Nb-O-Nb linkage within the square ring system. It is the fourth example of such a brick with niobium(V) synthesized in the presence of carboxylic acids. Previous studies reported a similar core, with different monocarboxylate linkers, such as methacrylate[38], acetate[44] and tertbutylacetate[45]. A related tetranuclear coordination complex was also described with salicylate groups associated with one hetero-element bismuth[40]. Due to the presence of bismuth, the off-planar benzene rings of the salicylate molecules are all located in one side of the tetranuclear core, and the alkoxyl molecules (isopropanol) are located on the opposite side. At last, this tetramer $\{Nb_4O_4\}$ is suggested in the work reported by Brown et al. as a possible analog of the parent tantalum(V) benzoate derivatives (benzoate, para-methylbenzoate and para-fluorobenzoate), but without any structural evidences for the niobium(V)-based complex[26].

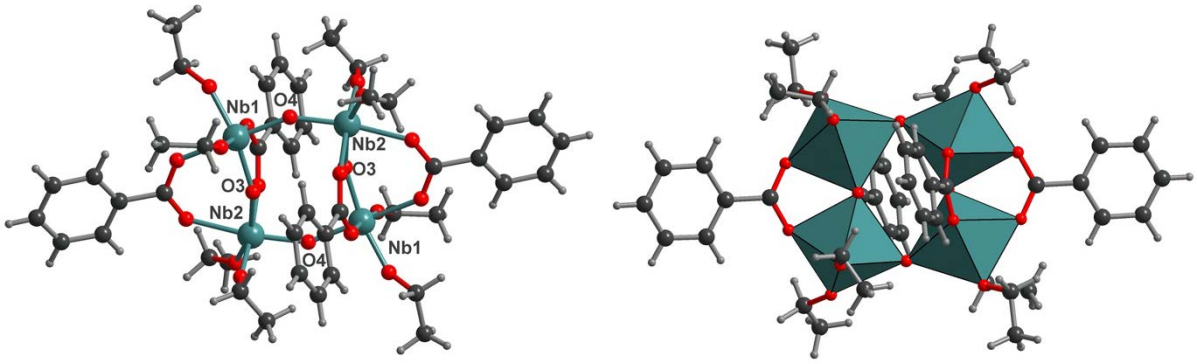


Figure 1: Ball and stick (top) and polyhedral (bottom) representations of the molecular tetranuclear coordination complex **1**. One of the ethoxy groups linked to Nb1 site (through Nb1-O8 bonding) is disordered on two equivalent positions. Only one of these ethoxy groups is shown for clarity.

Compound $[Nb_2(\mu_2\text{-}O)(C_{11}H_7O_2)_2(OEt)_6]$ (2)

The crystal structure of compound **2** is built up from one neutral molecular dinuclear species, containing two different crystallographically independent niobium(V) centers (Nb1 and Nb2), with a distorted octahedral geometry (Figure 2). Each of them is coordinated with the same configuration, three oxo groups from ethoxy molecules (Nb1-O_{Et} in the range 1.873(1)-1.880(1) Å; Nb2-O_{Et} in the range 1.865(2)-1.908(2) Å), two oxo groups from the carboxylate arm of the 2-naphtoate ligand (Nb1-O_c in the range 2.179(1)-2.195(1) Å; Nb2-O_c in the range 2.137(2)-2.156(1) Å) and one bridging μ_2-oxo groups with Nb1-O5 bond length of 1.930(1) Å and Nb2-O5 bond length of 1.908(1) Å. The occurrence of bridging μ_2-oxo species agrees well with bond valence calculations (1.958 for expected value of 2 for oxo)[43]. Within the dinuclear core, the niobium-centered octahedral polyhedra are sharing one corner, with a Nb1···Nb2 distance of 3.667(4) Å. The niobium atoms are further linked to each other through two bidentate carboxylate arms of the two distinct 2-naphtoate ligands, with a *syn-syn* bridging mode. The two 2-naphtoate molecules are located in a *cis* position, creating a tilting angle 145.7(8)° for

the Nb1-O5-Nb2 bonding. This arrangement is closely related to those encountered in the niobium(V) oxo-chloride [{$NbCl_3(C_7H_5O_2)$}$_2$(μ_2-O)] stabilized by two benzoate ligands[23] or in the niobium oxo-neopentyl alcohol [{$Nb(ONep)_3(C_5H_{10}O_2)$}$_2$(μ_2-O)] stabilized by two pivalate ligands[45]. Both monocarboxylate linkers adopt a similar bidentate bridging *cis* fashion: for the benzoate case, the Nb-O-Nb bridge was found to be bent with an angle of 143.2°, since it is 144.0(4)° for the pivalate case.

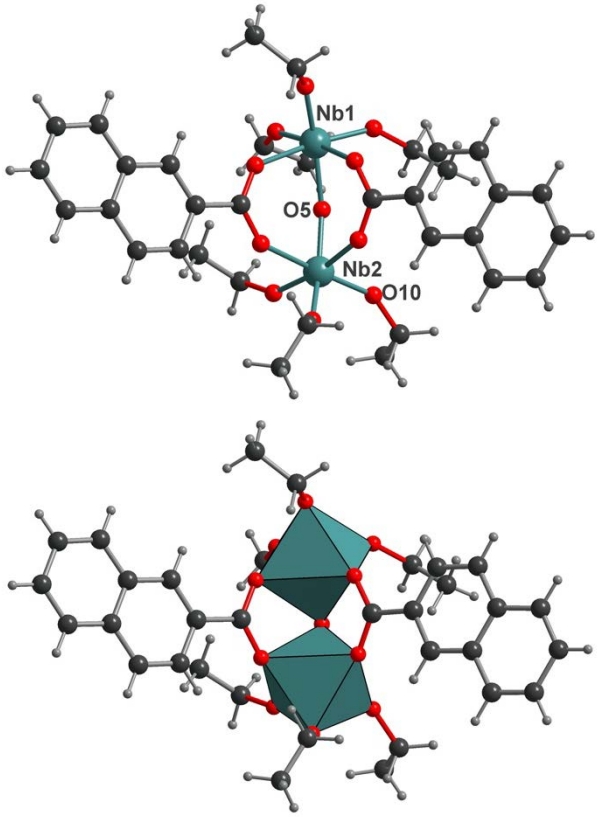


Figure 2: Ball and stick (top) and polyhedral (bottom) representations of the molecular dinuclear coordination complex **2**. One of the ethoxy groups linked to Nb2 site (through Nb2-O10 bonding) is disordered on two equivalent positions. Only one of these ethoxy groups is shown for clarity.

Compound [$Nb_2(\mu_2$-O)(μ_2-OEt)($C_{11}H_7O_2$)$(OEt)_6$] (3)

The compound **3** crystallizes in a non-centric space group $P2_12_12_1$, and exhibits a structure built up from two crystallographically independent niobium(V) centers, Nb1 & Nb2 (Figure 3). Both cations are octahedrally coordinated with three oxo groups from ethoxy molecules (Nb1-O_{Et} in the range 1.848(3)-1.903(4) Å; Nb2-O_{Et} in the range 1.878(4)-1.901(4) Å), one oxo groups from the carboxylate arm of the 1-naphtoate ligand (Nb1-$O1_c$ = 2.216(3) Å; Nb2-$O2_c$ = 2.204(2) Å), one bridging μ_2-ethoxy group with Nb1-O6 bond length of 2.130(4) Å and Nb2-O6 bond length of 2.128(4) Å, and one bridging μ_2-oxo groups with Nb1-O10 bond length of 1.952(4) Å and Nb2-O10 bond length of 1.918(5) Å. The bond valence of the μ_2-oxo species is 1.72, close to that of 2 expected for such species[43]. In this coordination complex, only one 1-naphthoate molecule is found and the carboxylate arm adopts a *syn-syn* bidentate bridging connecting mode with the two distinct niobium atoms Nb1 and Nb2. This configuration differs from the previous complex **2**, for which two 1-naphthoate ligands were observed in *cis* position. The occurrence of the single carboxylate bridge together with the bridging μ_2-ethoxy group induces a

shortening of the Nb1···Nb2 distance, which is 3.2277(10) Å, instead of 3.667(4) Å in the dinuclear core of compound **2**, and resulting in a tilting angle 113.0(2)° for the Nb1-O10-Nb2 bonding. The niobium-centered octahedral polyhedra are therefore linked through an edge-sharing mode via the μ_2-oxo and μ_2-ethoxy groups. The metric values of Nb···Nb lengths are smaller than those observed in the niobium-based dimeric moieties bearing two bridging alkoxides species, such as a μ_2-methoxy bridge (Nb···Nb = 3.493 Å[46]; Nb···Nb = 3.450 Å[47] or a μ_2-ethoxy bridge (Nb···Nb = 3.518 Å[39]. Indeed, the occurrence of the bridging μ_2-oxo group with smaller Nb-O bond distance decreases the Nb···Nb lengths in compound **3**, when an additional bridging μ_2-ethoxy group is present. At the opposite, the Nb···Nb lengths are increased when lacking the μ_2-ethoxy group, which are substituted by a second carboxylate pincer as found in the compound **2**. One may also notice that the Nb···Nb distance from edge-sharing {NbO_6} octahedra in the dense purely inorganic B form of Nb_2O_5[48], is 3.404 Å, and close to the value reported in the dimeric niobium alkoxides. It is interesting to notice that the position of carboxylate arm on the naphthalene group induces either a monocarboxylate coordination complex in compound **3** (position 1) or a dicarboxylate coordination complex in compound **2** (position 2).

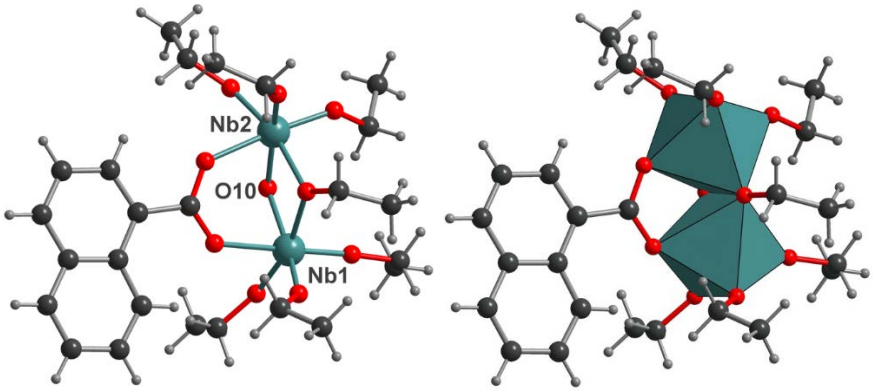


Figure 3: Ball and stick (top) and polyhedral (bottom) representations of the molecular dinuclear coordination complex **3**.

Compound $[Nb_2(\mu_2\text{-}O)(C_{14}H_{11}O_2)_2(OEt)_6]$ (4)

The crystal structure of compound **4** exhibits the same dinuclear motif (Figure 4) as found for compound **2**, except that the centrosymmetric molecular moiety results in only one crystallographically independent niobium(V) center (Nb1). The latter is octahedrally coordinated through three oxo groups from ethoxy molecules, with Nb1-O_{Et} bond distances varying from 1.868(2) Å to 1.887(2) Å, two oxo groups from carboxylate arms (Nb1-$O1_c$ = 2.167(2) Å and Nb1-$O2_c$ = 2.169(2) Å), and one bridging μ_2-oxo group (Nb1-O3 = 1.914(1) Å). The bond valence calculation for this oxygen O3 atom gives the value of 1.984, in agreement with the occurrence of an oxo group[43]. The oxygen O3 atom sits on the special position 4*e* (axis 2 point symmetry), resulting in two equivalent niobium atoms forming the dimeric unit, in which the Nb1···Nb1 distance is 3.645(2) Å, related to the tilting angle of 144.42(2)° for the Nb1-O3-Nb1 bonding. As for compound **2**, two carboxylate groups from two distinct 4-methyl-biphenylmonocarboxylate ligands are linked to the two adjacent niobium (Nb1) centers, in a *syn-syn* bidentate bridging fashion, and adopting a *cis* position.

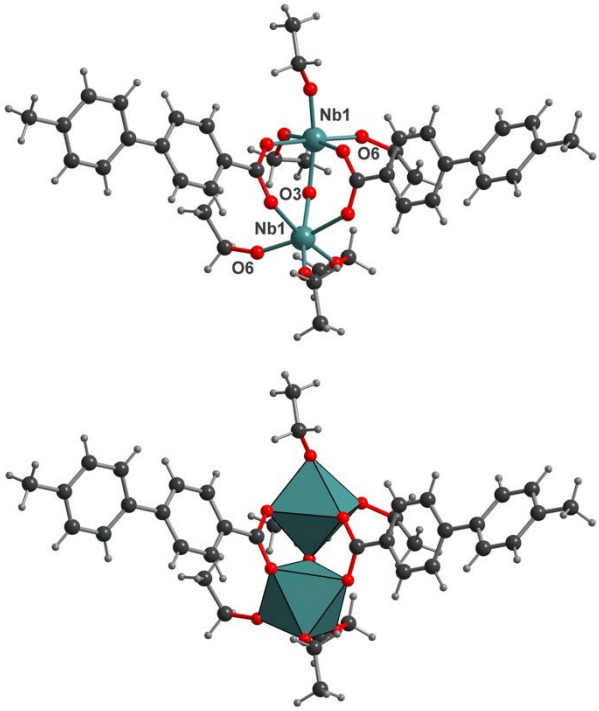


Figure 4: Ball and stick (top) and polyhedral (bottom) representations of the molecular dinuclear coordination complex **4**. One of the ethoxy groups linked to Nb1 site (through Nb1-O6 bonding) is disordered on two equivalent positions. Only one of these ethoxy groups is shown for clarity.

Compound $[Nb_2(\mu_2\text{-}O)(\mu_2\text{-}OEt)(C_{15}H_9O_2)(OEt)_6]_2$ (5)

The crystal structure of compound **5** is built up from two crystallographically independent motifs containing two distinct niobium(V) sites (Nb1 & Nb2 and Nb3 & Nb4), linked to each other through one μ_2-oxo and one μ_2-ethoxy groups, and one carboxylate arm of the 9-anthracenecarboxylate ligand (Figure 5). The existence of only one carboxylate molecule within such a dinuclear niobium core is similar to that encountered in compound **3**, obtained with 1-naphthoic acid. The 9-anthracenecarboxylate ligand acts as *syn-syn* bidentate linker with two adjacent niobium atoms (either Nb1 & Nb2 or Nb3 & Nb4). The four niobium centers are typically octahedrally coordinated with an identical geometrical environment. They are bound to one μ_2-oxo group (Nb1-O3 = 1.934(1) Å; Nb2-O3 = 1.937(1) Å; Nb3-O13 = 1.939(2) Å; Nb4-O13 = 1.936(2) Å), one bridging μ_2-ethoxy group (Nb1-$O4_{Et}$ = 2.128(1) Å; Nb2-$O4_{Et}$ = 2.121(1) Å; Nb3-$O14_{Et}$ = 2.126(1) Å; Nb4-$O14_{Et}$ = 2.1148(1) Å), one oxo group from the carboxylate arm of the 9-anthracenecarboxylate ligand (Nb1-$O1_c$ = 2.196(1) Å; Nb2-$O2_c$ = 2.181(1) Å; Nb3-$O12_c$ = 2.205(1) Å; Nb4-$O11_c$ = 2.191(1) Å), and three oxo groups from ethoxy molecules (Nb-O_{Et} in the range 1.855(2)-1.917(2) Å). The calculated bond valences of the μ_2-oxo group bridging the two niobium centers are 1.872 for O3 and 1.862 for O13, in agreement with the occurrence of an oxo group[43]. As observed in the dinuclear unit in compound **3**, we observe that the niobium atoms are connected through only one carboxylate pincer in compound **5**, resulting in an additional bridging μ_2-ethoxy group. In compounds **2-4**, this μ_2-ethoxy group was not present and substituted by a second carboxylate bridge from a second organic linker. For **5**, the niobium-centered octahedral polyhedra are therefore linked through an edge-sharing mode via the two μ_2-oxo ligands (oxo and ethoxy), corresponding to

a shorter Nb1···Nb2 and Nb3···Nb4 distances of 3.2283(3) Å and 3.2561(3) Å, respectively. Related Nb-O-Nb bond angles are also lower, with value of 113.01(7)° and 114.37(8)° for the set Nb1-Nb2 and Nb3-Nb4, respectively. Similar metric values were observed in compound **3**. The crystal structure packing of compound **5** results from the molecular assemblies of two neutral dinuclear units with 9-anthracenecarboxylate, which differ only by the disorder of some ethoxy groups linked to the niobium centers. There exist one disordered ethoxy group for the Nb1-Nb2 set whereas there are three disordered ethoxy groups for the Nb3-Nb4 set.

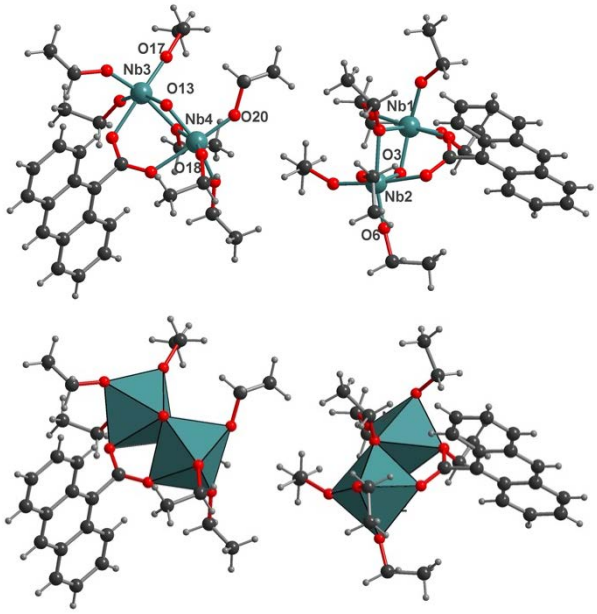


Figure 5: Ball and stick (top) and polyhedral (bottom) representations of the molecular coordination complex **5**. For one molecule, one of the ethoxy groups linked to Nb2 site (through Nb2-O6 bonding) is disordered on two equivalent positions. The same configuration occurs for the Nb3 and Nb4 sites of the second molecule with three disordered ethoxy groups (through Nb3-O17, Nb4-O18 and Nb4-O20 bondings). Only one of these ethoxy groups is shown for clarity.

Compound $[Nb_2(\mu_2\text{-}O)(C_{15}H_9O_2)_2(O^iPr)_6]_2$ (6)

With the 9-anthracenecarboxylic acid (with starting molar ratio of 0.375 carboxylic acid ligand for 1 niobium precursor; 0.333 carboxylic acid for 1 niobium in compound **5**), a new type of crystalline product appeared, as compound **6**, when adding isopropanol as solvent in the reaction medium. Its crystal structure is closely related to those observed in compounds **2** and **4**, and contains a centrosymmetric dinuclear core with one crystallographic unique niobium(V) atom (Nb1) and two bridging 9-anthracenecarboxylate species (Figure 6). This cation is octahedrally coordinated with three oxo groups from isopropoxy molecules, with Nb1-O_{Pr} bond distances varying from 1.863(2) Å to 1.880(2) Å, two oxo groups from carboxylate arms (Nb1-$O1_c$ = 2.175(2) Å and Nb1-$O2_c$ = 2.219(2) Å), and one bridging μ_2-oxo group (Nb1-O3 = 1.9103(6) Å). The bond valence calculation for this oxygen O3 atom gives the value of 2.038, in agreement with the occurrence of an oxo group[43]. Within the dinuclear core, two niobium centers are linked through two carboxylate arms from two distinct 9-anthracenecarboxylate ligands and one bridging μ_2-oxo group (on special position 4*e*), generating a Nb1···Nb1 distance of 3.664(5) Å and a tilting Nb1-O3-Nb1 angle of 147.1(1)°, as found in the similar coordination complexes **2** and **4**. The two 9-anthracenecarboxylate ligands bridge two niobium atoms as *syn-syn* bidentating fashion. However, the terminal ethoxy groups occurring the

compounds **1-5** have been substituted by isopropoxy ligands, some of which occupy two disordering positions (through O6 atom; Figure 6).

From the observation in compound **6**, we were able to synthesize different coordination complexes with a dinuclear niobium core associating bulky anthracene moiety, with two distinct Nb/L ratio of 2/1 and 2/2 by playing on the addition of alcohol solvent. These results seem to indicate that the Nb/L ratio would be controlled by the initial carboxylic acid content rather that its steric hindrance.

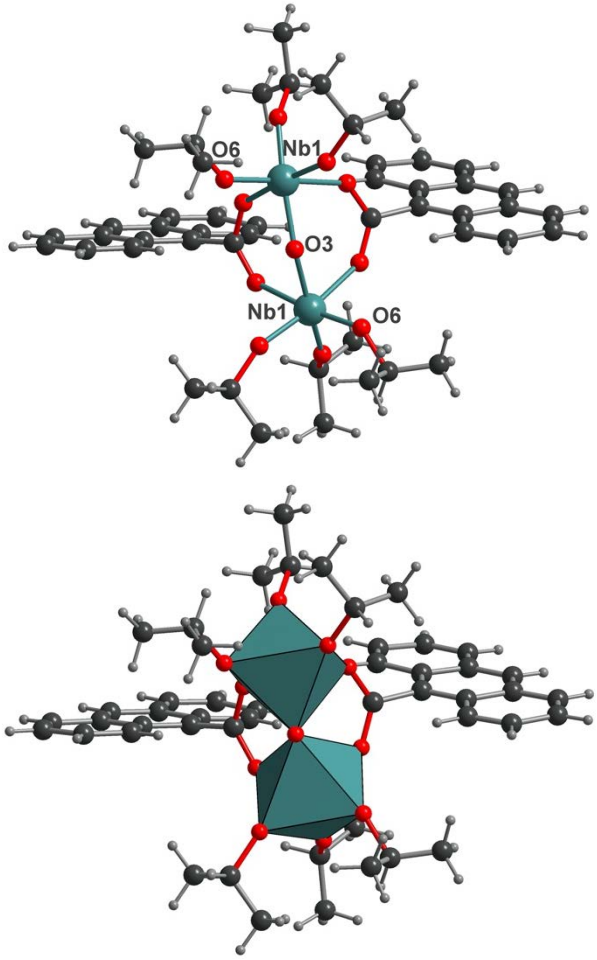


Figure 6: Ball and stick (top) and polyhedral (bottom) representations of the molecular dinuclear coordination complex **6**. One of the isopropoxy groups linked to Nb1 site (through Nb1-O6 bonding) is disordered on two equivalent positions. For them, the methyl groups is located on two close equivalent positions with occupancy 53/47. Only two of the four methyl groups are shown for clarity.

Compound $[Nb_4(\mu_2\text{-}O)_4(C_{11}H_7O_2)_4(OEt)_8]$ (7)

Compound **7** is the second complex synthesized with the 2-naphthoic acid (see compound **2**). Its crystal structure is closely related to that of the tetranuclear niobium(V)-centered $\{Nb_4O_4\}$ motif stabilized by benzoates species (compound **2**), except that the latter ligand is substituted by the 2-naphthoate molecules (Figure 7). It is built up from two inequivalent niobium(V) atoms (Nb1 & Nb2) linked to each other via μ_2-oxo groups (O7 and O8), within a square-ring unit. Each niobium center is octahedrally coordinated by two μ_2-oxo groups (Nb1-O7 = 1.908(4) Å, Nb1-O8 = 1.919(4) Å; Nb2-O7 = 1.895(4) Å, Nb2-O8 = 1.921(3) Å), two oxygen atoms from ethoxy groups (Nb1-O_{Et} = 1.858(4)-1.879(4) Å; Nb2-O_{Et} = 1.869(4)-1.885(3) Å), and two

carboxyl oxygen atoms belonging to the 2-naphthoate ligand (Nb1-O_c = 2.157(3)-2.163(4) Å; Nb2-O_c = 2.167(4)-2.176(4) Å). The bond valence calculation for the μ_2-oxygen atoms O7 and O8 gives the value of 1.987 and 2.017, respectively, in agreement with the occurrence of an oxo group[43]. There occur two types of 2-naphthoate molecules acting through the carboxylate arm as a *syn-syn* bidentate bridging connecting mode with the two distinct niobium atoms Nb1 and Nb2. They are located in *cis* position related to the Nb1-O8-Nb2 linkage, which is characterized by a bonding angle of 145.9(2)°. The other Nb1-O7-Nb2 bond angle is slightly larger with a value of 152.5(2)°. These metric values are similar to those found the other tetrameric brick observed with benzoate ligands (compound **1**), with the same alternation of concave and convex bending of Nb1-(μ_2-O)-Nb2 bondings. Within the tetramer, the Nb1⋯Nb2 bond lengths are in the range 3.672(2)-3.694(1) Å. The dihedral angle of the two naphthalene rings is nearly perpendicular, with a value of 89.7(2)°, with one naphthalene pointing toward along the {Nb_4O_4} tetramer plane and the second one upward and downward to this {Nb_4O_4} plane. In this series, this value is the lowest one, since all other complexes involving dinuclear niobium-centered units with two carboxylate ligands, or tetranuclear niobium-centered units, exhibit an angle ranging from 100.92(4)° (compound **4**) up to 118.92(5)° (compound **2**), indicating a more opened angle for *cis* conformation of the carboxylate linkers. Indeed, this dihedral value is much lower that reported in the tetramer (112.8°) with benzoate ligands (compound 1). The {Nb_4O_4} motif is then further decorated with eight ethoxy groups pointing perpendicularly to the plane formed by the naphthalene groups.

The observation of two nuclearities of niobium complexes was not reported for a given carboxylate ligand, since either dinuclear or (not and) tetranuclear entity was reported in literature. Indeed, it was proposed that steric hindrance of the ligand might orientate the nuclearity of the complex as illustrated in the work of Boyle, for which a dimer was obtained with a bulky molecule (pivalic acid), whereas a tetramer is obtained with a less bulky molecule (terbutylacetic acid), prepared in the same synthetic conditions. In fact, by using 2-naphthoic acid, we show here that the nuclearity of the inorganic core is controlled by the hydrolysis rate. For a low water content (coming from esterification reaction), the dinuclear core {Nb_2O} is observed, whereas the tetranuclear core {Nb_4O_4} is obtained in a closed reaction medium (desiccator) saturated with 55% water humidity, coming from a saturated solution of Na_2CO_3.

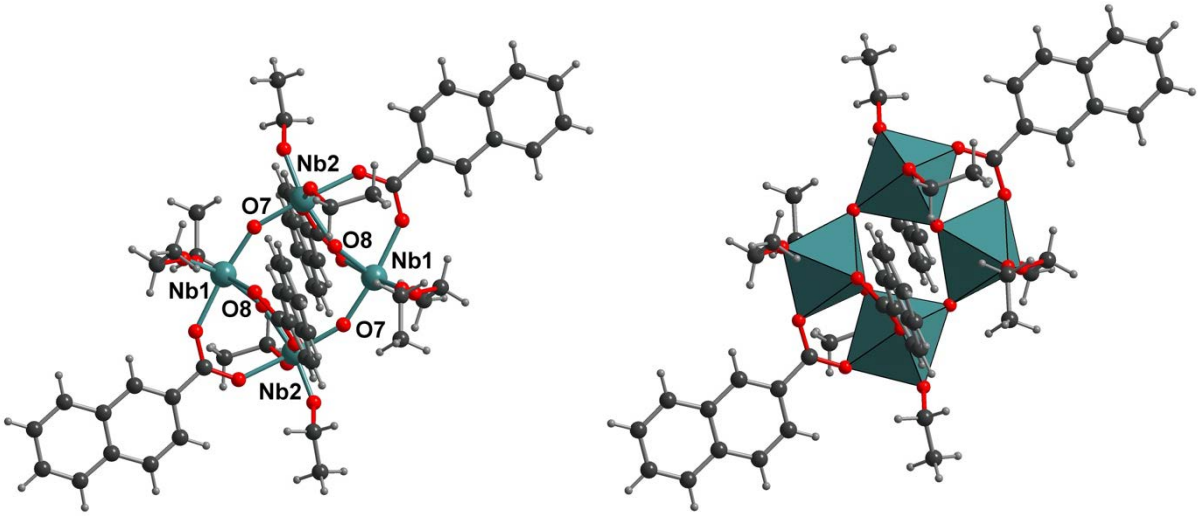


Figure 7: Ball and stick (top) and polyhedral (bottom) representations of the molecular tetranuclear coordination complex **7**. One of the ethoxy groups linked to Nb1 site (through Nb1-O10 bonding) and Nb2 site (through Nb2-O7 bonding), is disordered on two equivalent positions. Only one of these ethoxy groups is shown for clarity.

Compound $[Nb_8(\mu_2\text{-}O)_{12}(C_{11}H_7O_2)_8(\eta_1\text{-}C_{11}H_7O_2)_4(OEt)_4]\cdot[Nb_8(\mu_2\text{-}O)_{12}(C_{11}H_7O_2)_8(\eta_1\text{-}C_{11}H_7O_2)_2(OEt)_6]$ (8)

Compound **8** is the third niobium-centered complex isolated by means of the 2-naphthoate ligand (see compounds **2** and **7**). Its crystal structure is built up from two distinct neutral molecular entities (noted A and B), containing both eight niobium centers, with similar connection modes consisting of twelve bridging μ_2-oxo groups (Figure 8). The two arrangements can be viewed as the condensation of two niobium-centered tetranuclear bricks (related to those encountered in compounds **7** and **1**) through four additional μ_2-oxo groups, located perpendicularly to its square plane of Nb-O-Nb bondings. It results in a cubic octanuclear core $\{Nb_8O_{12}\}$, where the niobium atoms occupy the eight corners, and the bridging μ_2-oxo groups are located nearby the twelve edges. For each octameric entities A and B, there exist four crystallographic inequivalent niobium atoms, which are octahedrally coordinated to three μ_2-oxo groups, two carboxyl oxygen atoms belonging to the 2-naphthoate ligand (in bidentate *syn-syn* bridging mode between two adjacent Nb) and one remaining oxygen atoms from either ethoxy groups or monodentate 2-naphthoate ligand. The Nb-O_{oxo} bond distances are in the range 1.825(9) - 1.967(9) Å for core A and 1.835(7) - 1.969(6) Å for core B, whereas the Nb-O_c (from the bidentate 2-naphthoate ligand) are in the range 2.092(7) - 2.196(10) Å for core A and 2.132(8) - 2.175(11) Å for core B. The bond valence calculations for the twelve μ_2-oxygen atoms O1A-O6A and O1B-O6B, from the molecules A and B, corresponds to the values range of 2.022 - 2.122 and 1.979-2.083, respectively, in agreement with the occurrence of an oxo group[43]. The last Nb-O bond lengths related to the ethoxy or monodentate naphthoate (η_1) ligands are observed in the range 1.941(14)-2.009(15) Å for core A and 1.927(7) - 2.022(13) Å for core B. For molecule A, the Nb-O-Nb bonding angles vary from 143.5(4)° to 147.7(4)°, whereas they vary from 142.6(4)° to 150.6(4)° for molecule B. Within the octamer A, the Nb···Nb bond distances are in the range 3.672(2)-3.694(1) Å and they are in the range 3.672(2)-3.694(1) Å for the octamer B. For the bidentate 2-naphtoate ligands, we observe dihedral angles between the naphthalene rings, nearly perpendicular, with values 85.2(6)-86.6(6)° for molecule A and 84.1(2)-86.3(4)° for molecule B. It results that the naphthalene rings pointed out in the (*a*,*c*) plane, with pairs of adjacent aromatic molecules, which exhibit typical π-π interactions, as reveal the $C_{ar}\cdots C_{ar}$ (C_{ar} = aromatic carbon) distances close to 3.6-3.7 Å. Moreover, weaker π-π interactions also occur between the naphthalene rings ($C_{ar}\cdots C_{ar}$ of 3.7-4.0 Å length) belonging to two distinct neighboring octanuclear cores, which ensure the structural cohesion in the [100] and [001] directions. The two entities A and B only differ by the nature of terminal ligands via oxo groups attached to niobium centers, which are four ethoxy groups and four monodentate 2-naphtoate groups for A, and six ethoxy groups and two monodentate 2-naphtoate groups for A. These naphthalene monocarboxyl species exist under its non-protonated form, with short non-bonded C-O distances in the range ≈ 1.16(3)-1.24(2) Å, relating to the C=O linkage. An infrared vibration band at 1670 cm^{-1} (Table 2; Figure S3h) is visible and attributed to such configuration of monodentate naphthoate linker. Indeed, it is the first example in our work of the substitution of ethoxy groups by monodentate carboxylic acids,

with variable contents (either 4 EtO / 4 naphthoate or 6 EtO / 2 naphthoate), leading to a complex molecular assembly of octanuclear niobium cores. The other originality of this polynuclear niobium(V) brick is the number of the eight metallic 4*d* centers, engaged in a cubic configuration, which has not previously been reported in literature. Only a closely related octanuclear building block was described with the parent pentavalent tantalum(V), in the complex $[Ta_8(O)_{12}(O_2CNEt)_2)_{16}]$.[49] The latter brick is stabilized by the 16 *N*,*N*-diethylcarbamato ligands which act either as monodentate and bridging bidentate connection mode.

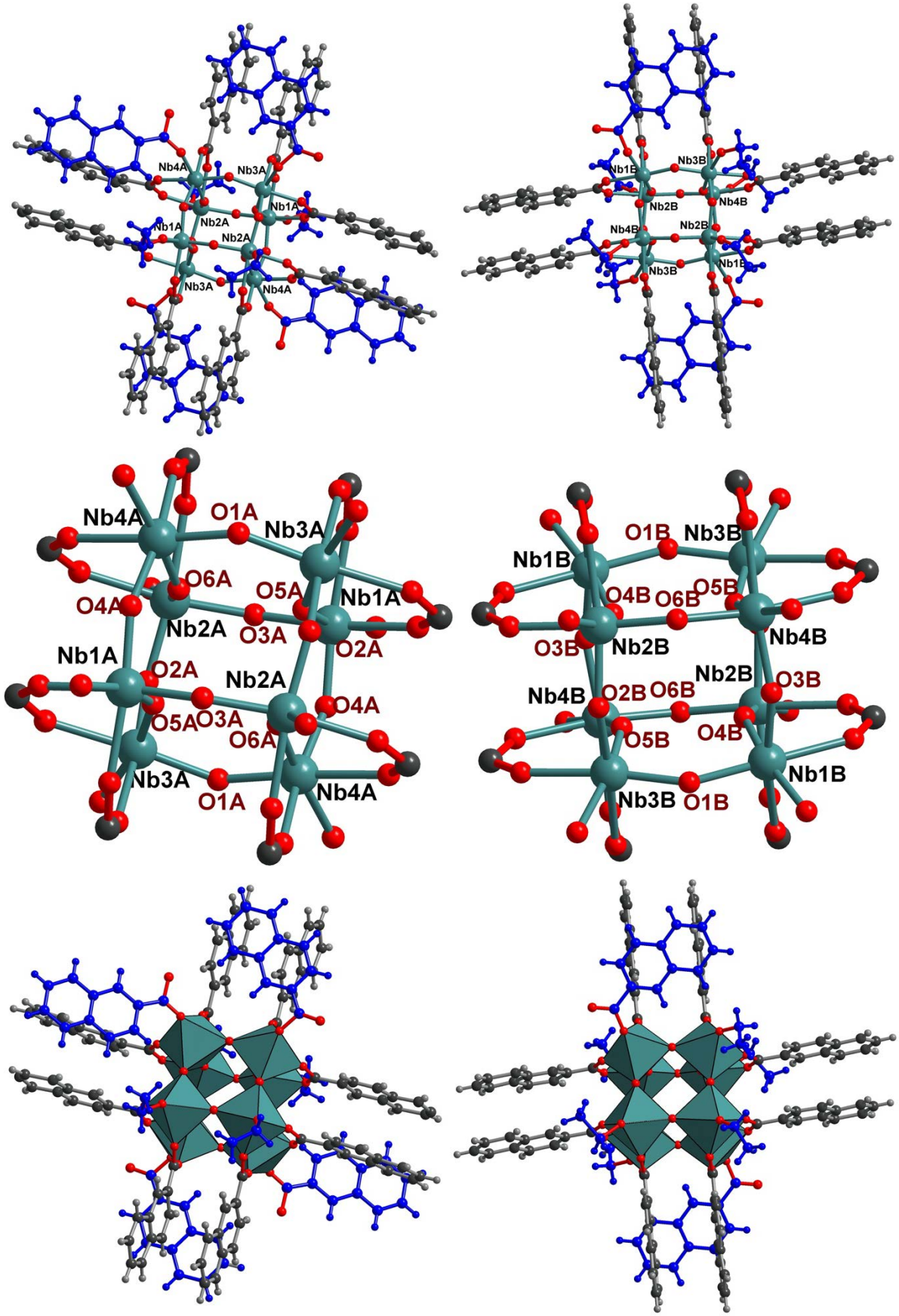


Figure 8: Ball and stick (top) and polyhedral (bottom) representations of the molecular octanuclear coordination complex **8**. The latter consists of two distinct inequivalent entities which contains either 4 ethoxy groups / 4 monodentate 2-naphthoate groups (Molecule A - left) or 6 ethoxy groups / 2 monodentate 2-naphthoate groups

(Molecule B - right). These terminal ethoxy or monodentate 2-naphthoate groups are indicated in blue, for a better clarity of the representation.

Infrared spectroscopy

We investigated the different niobium(V) ethoxide – carboxylic acid systems by infrared spectroscopy, in order to characterize the crystallization of the complexes **1**-**8**. After the thermal treatment for the formation of complexes **7** and **8**, no supernatant was obtained due to the large amount of organic ligand that recrystallized once they cooled down. For each batch (except for compounds **7** and **8**, for which no supernatant is obtained), 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 (variable times depending on the crystallization duration for a given complex). Distinct zones are of interest and attributed to the ethoxide (or isopropoxide for complex **5**) group[50]. The 3050-2750 cm^{-1} range is of interest and related to the ν(C-H) stretching vibrations of the ethyl groups (with typical bands at ≈ $2970_{(asym)}$ and ≈ $2860_{(sym)}$ cm^{-1}), and the 1480-1370 cm^{-1} zone related to the ν(C-H) bending vibrations of the methyl groups (with typical bands at 1470-1404 and 1375 cm^{-1}). The bands at around 1200-1000 cm^{-1} are assigned to the ν(C-O) vibrations coming from the ethoxide group linked to niobium center, via Nb-O-C_{Et} linkage: typical peaks are found at 1100-1090 cm^{-1} and 1060-1050 cm^{-1}. The broad peak at around 573-529 cm^{-1} are related to ν(Nb-O) stretching modes[51]. These different signatures are observed either in the supernatant solution or in 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 the complexes **2**-**6** (and **7** for only before thermal treatment), we observed the same trends (Figures S3b-S3g), since unprotonated carboxylate ligands are always visible in the supernatant solutions after mixing the chemical reactants (see Table 1). Indeed, for complex **2** system, the band at 1683 cm^{-1}, is related to the ν(C=O) stretching from 2-naphtoic acid, but disappears when it is mixed with the niobium ethoxide solution. The corresponding vibration stretching is shifted to 1599 cm^{-1} and 1551 cm^{-1}, related to the ν_{asym}(COO) and ν_{sym}(COO), respectively, revealing the bonding between carboxylate group and niobium centers[44] in supernatant solution, just after 1h mixing. This observation indicates the relative 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. This group of two peaks are also found in the solid-state form of the crystalline coordination complex of **2** (at 1598 cm^{-1} and 1560 cm^{-1}). This reactivity of the carboxylic acid toward the niobium ethoxide is observed for the different crystallization processes for complexes **2**-**7**. However, infrared signatures differ for some supernatant solution samples after crystallization, since some of them only show very weak bands related to ν(C-OO) vibrations, corresponding to a smaller content of niobium carboxylate complex in the final solution. This evolution is attributed to the transfer of “soluble” niobium-ethoxide-carboxylate complex into the solid crystalline form. This is

clearly the case for the crystallization of complex **3** (with 1-naphthoic acid, after 6 months), or in a less extend, for complexes **4** (with 4-methylbiphenylcarboxylic acid, after 3 weeks) and **5** (with anthracene-9-carboxylic acid, after 2 weeks), for instance.

The formation of the complex **1** with benzoic acid, shows the same behavior, with the band of the carboxylic function at 1680 cm^{-1} (ν(C=O)) shifting to 1598 and 1560-1556 cm^{-1} (ν(COO)) when mixed with the niobium ethoxide precursor. It is related to its unprotonated state, either in supernatant solution and solid-state crystallized form, indicating the carboxylate complexation with niobium cations. However, a new group of bands is appeared in the range 1722-1698 cm^{-1} in the supernatant solution (Figure S3a), either after 1h mixing or 1-month crystallization, and is assigned to the ν(C=O) coming from the formation of ethyl-benzoate ester. Similar reaction has been previously described for the synthesis of the tetranuclear niobium acetate complex[44]. The formation of such basic ester organic molecule is expected in such a mixture involving the reaction between a carboxylic acid and an alcohol. The latter will come from proton exchange between the benzoic acid and the attached ethoxide group from niobium alkoxide precursor. This results in the complexation of benzoate with niobium (as indicated by the IR bands of the ν(COO) vibrations) and a leaving group of ethanol species, which further react with benzoic acid, present in excess in the starting mixture. It is noticed that the bands attributed to the ethylbenzoate ester is not visible for the crystalline complex **1**, and occurs only in the solution. However, such ester molecules have not been detected in the other niobium-carboxylic acid system, which could be due the sensitivity of the IR technique. Thus, the formation of the ester molecules with the systems involving other carboxylic acids has been then investigated by liquid ^{1}H NMR of the supernatant solution.

Table 1. Comparison of the ν(C=O) vibrations (from carboxylic acid function) and ν(COO) vibrations (from carboxylate function) for the complexes **1**-**8** (in cm^{-1}).

		$\nu(C=O)_{acid}$	$\nu_{asym}(COO)$	$\nu_{sym}(COO)$
Complex 1	benzoic acid	1680	/	/
	supernatant (1 hour)	/	1598	1556
	supernatant (1 month)	/	1599	1560
	crystalline product	/	1598	1560
Complex 2	2-naphtoic acid	1683	/	/
	supernatant (1 hour)	/	1599	1551
	supernatant (5 days)	/	1600-1587	1560
	crystalline product	/	1598	1560
Complex 3	1-naphtoic acid	1670	/	/
	supernatant (1hour)	/	1596	1543
	supernatant (1 months)	/	n.o.*	n.o.[a]
	crystalline product	/	1597	1537
Complex 4	4-methylbiphenylcarboxylic acid	1678	/	/
	supernatant (1 hour)	/	1592	1537
	supernatant (3 weeks)	/	1591 (weak)	1535 (weak)
	crystalline product	/	1598	1561
Complex 5	anthracene-9-carboxylic acid	1678	/	/
	supernatant (1 hour)	/	1594	1540
	supernatant (2 weeks)	/	n.o.*	n.o.[a]
	crystalline product	/	1597	1561
Complex 6	anthracene-9-carboxylic acid	1682	/	/
	supernatant (1 hour)	/	1554	n.o.[a]
	supernatant (2 weeks)	/	1557 (weak)	n.o.[a]
	crystalline product	/	1584	1527
Complex 7	2-naphtoic acid	1683	/	/
	supernatant (1 hour)	/	1597	1550

	crystalline product	/	1598	1557
Complex 8	2-naphtoic acid	1683	/	/
	crystalline product	/	1670[b] & 1586	1548

[a]n.o. : not observed. [b] from monodentate naphthoate species.

Liquid NMR ^{1}H (and 2D ^{13}C-^{1}H) of supernatants for complexes 1, 2 and 4

Nuclear magnetic resonance was chosen as a more informative technique in order to investigate the presence of the ester in the supernatant of each reaction batch. As mentioned before, the presence of these ester functions is a condition to form in-situ water molecules able to condense, in a controlled way, the niobium cations to each other through bridging oxo ligands, and form polynuclear species. Since the niobium precursor {$Nb(OEt)_5$} is a liquid, its ^{1}H-NMR spectrum has been recorded too, revealing a quartet centered at 5.035 ppm which is attributed to the two protons of -CH_2- and a triplet at 1.83 ppm attributed to the three protons of -CH_3 (Figure S4a). At 4.82 ppm another broad peak is observed which can derive from the existence of two different -CH_2- groups, either terminal or bridging in the dimeric {$Nb_2(\mu^2\text{-}OEt)_2(OEt)_8$} precursor. Indeed, the integration matches with this hypothesis and we can assume that the 8 terminal -CH_2- give the quartet at 5.035 ppm and the 2 bridging ones the broad signal at 4.82 ppm. However, in the case of -CH_3 groups belonging to the bridging ethoxy ligand, a signal is not clearly observed. One can assume that, due to the higher distances of the -CH_3 groups from the niobium centers, there are no significant differences in the chemical shifts those belonging to terminal and bridging ethoxy ligand so that both signals appear overlapped.

Among the eight systems giving rise to crystalline products, we selected three of them (**1**, **2** and **4**), for which clear liquid ^{1}H NMR signatures can be extracted from the supernatant solution, without significant perturbation of overlapping peaks due to the complexity of some carboxylic acid ligands in the aromatic region. For each reaction leading to the compounds **1**, **2** and **4**, supernatant ^{1}H-NMR experiments were conducted before and after the crystallization process to follow the formation of the ethyl ester species. As “before crystallization” we define the time for which the ligand solubilizes totally into the niobium(V)ethoxide precursor (approximately 1 hour) and as “after crystallization”, we define the time after the appearance of crystals (reaction time ranging from 5 days (**2**), 7 days (**4**) and 1 month (**1**)).

We first describe in detail the results for compound **2** (involving 2-naphthoic acid) as the best resolved system. Before crystallization, we observe expected ^{1}H NMR signals located in the aromatic region (from 7 to 9 ppm), and aliphatic region (from 0 to 5 ppm; Figure 9, top). For the for 2-naphthoic acid, the protons H1 and H2 show a singlet at 9.20 ppm and a doublet at 8.70 ppm respectively. The rest of the aromatic protons resonates at 8.46 ppm (doublet, H3), 8.40 ppm (multiplet, H4 and H7) and at 8.07 ppm (multiplet, H5 and H6). The signature of the ethoxy group of the niobium ethoxide precursor, appears with a weak shielding of the chemical shifts (at 4.98 ppm for -CH_2- groups and 1.77 ppm for -CH_3 groups), compared to the free niobium ethoxide precursor (Figure S4a). It is worth noting that we still observed the presence of the terminal and bridging ethoxide groups generating the broad signal at 4.98 ppm and 4.76 ppm respectively

After the crystallization, the ^{1}H-NMR spectrum of supernatant is more complex indicating that a reaction occurred between the 2-naphtoic ligand and the niobium ethoxide precursor (Figure 9, bottom). It was clearly observed a mixture of 2-naphthoic acid species (noted A), an ethyl-

naphthoate ester form (noted B) and likely naphthoate ligand interacting with niobium centers prior to their crystallization (noted C). For these three species, the aromatic part of the ligand remains unchanged and should generate an identical number of ^{1}H signals but, different chemical shifts are observed due to the different chemical configurations. In the aromatic region, the H1 atom is firstly considered as isolated (one singlet for the starting solution (Figure Figure 9, top), but it is seen as three singlet signals corresponding to the three different configurations of naphthoates species, A, B and C.

To discriminate them, a ^{13}C-^{1}H HMBC (Heteronuclear Multiple Bond Correlation) 2D experiment was performed (Figure 10). This method gives correlations between carbons and protons that are separated by two, three, and, sometimes in conjugated systems, four bonds. From this analysis, we assign the signal located at 8.85 ppm to the ester form (B) as it is correlated to the carbon atom $C1_B$ (carbon in 1 position for the naphthalene part of molecule B) bearing the $H1_B$ proton with the -CH_2- group of the ethyl group, centered at 4.71 ppm. The two remaining singlet signals correspond to the naphthoic acid, $H1_A$ at 8.94 ppm and $H1_C$ at 9.06 ppm, respectively. The latter has a weaker intensity because it is involved during the solid-state crystal growth of complex **2**, and thus a lower concentration in supernatant solution. This observation regarding the differentiation between A and C species is confirmed by a DOSY experiment performed on the supernatant after crystallization (Figure S4b). For the aromatic region of the spectrum, we clearly see the presence of the three different forms with diffusion values of 4.95 x 10^{-10} m^2/s, 6.27 x 10^{-10} m^2/s and 2.55 x 10^{-10} m^2/s related to species A, B and C, respectively. As diffusion parameter is related to the size of a given molecule in solution, the lower diffusion value (2.55 x 10^{-10} m^2/s) is related to the naphthoate ligand interacting with the niobium centers (C). The remaining naphthoic acid (A) has thus a diffusion value of 4.95 x 10^{-10} m^2/s. The latter appears to be smaller than the ester form (B) probably because of dimerization by COOH···COOH interactions in the supernatant, resulting in a bigger hindrance for the (A) form than that of ester form (B).

The second set of signals between 8.25 ppm and 8.6 ppm appears as three doublets standing for the H2 hydrogen. Accordingly, with the determination of the three-singlets H1, the three H2 doublet signals centered at 8.29 ppm, 8.40 ppm and 8.54 ppm are attributed to $H2_B$, $H2_A$ and $H2_C$, with the same C, A, B order, respectively. $H2_B$ is further confirmed by the ^{13}C-^{1}H HMBC measurement (Figure 10) as it interacts with the -CH_2- ethyl signal located at 4.71 ppm. The signals corresponding to the other protons (H3-7) are heavily overlapped and resonate as two multiplets centered at 8.18 ppm and 7.81 ppm. It may be caused by their location, far from the carboxylate function. No HMBC correlation is observed for these protons. The free niobium ethoxide precursor pics are also visible at 5.88 ppm, 3.98 ppm and 1.54 ppm.

For the aliphatic region, signals of the protons of the ester, -CH_2- that resonate at 4.72 ppm (quartet circled in red) and -CH_3- that resonate at 1.71 ppm (triplet circled in blue) belong also to the 2-ethylnaphthoate ester form (B). Moreover, we observe a broad singlet deriving at 5.88 ppm coming from the released ethanol molecules (green box on figure 9).

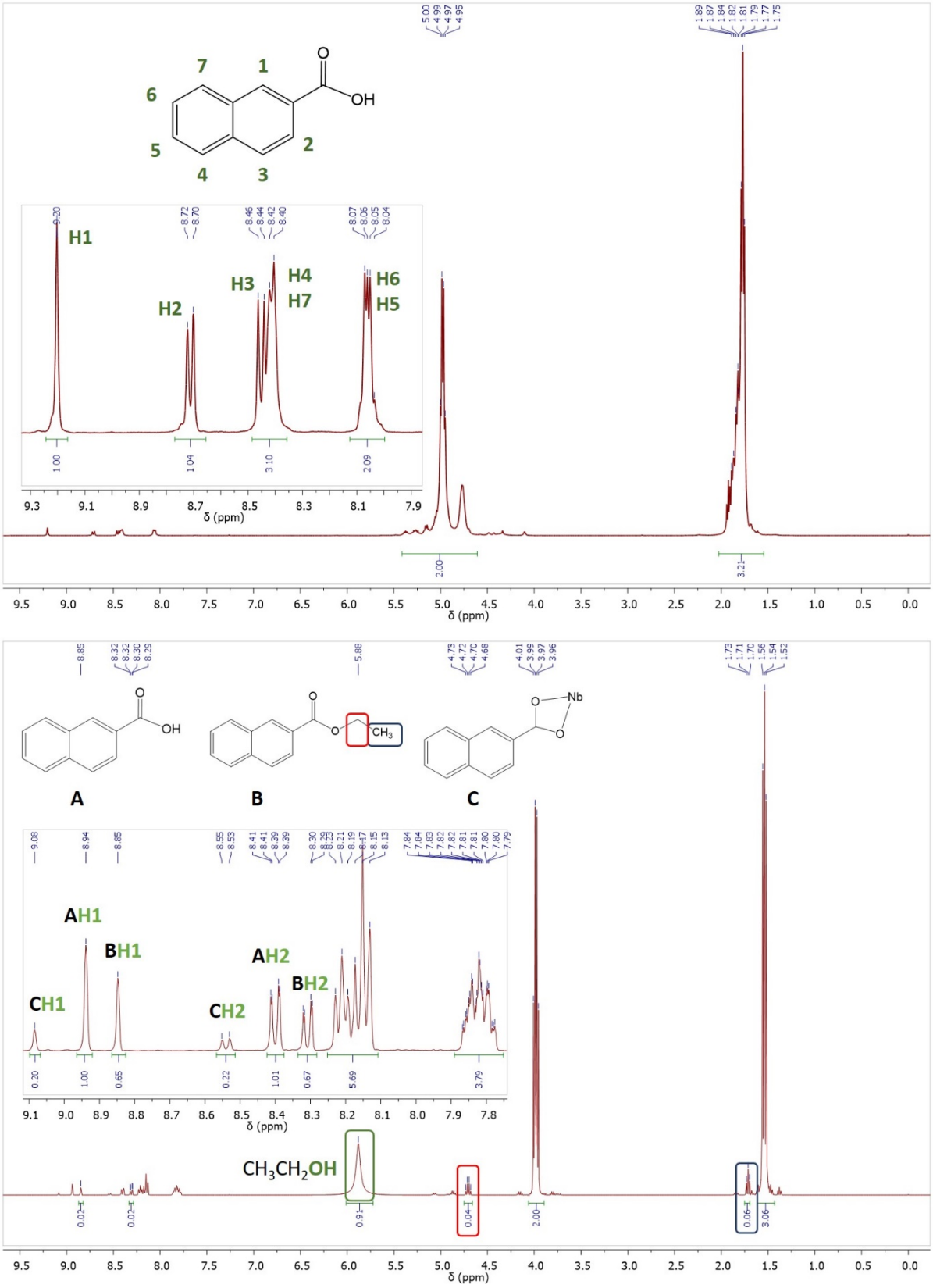


Figure 9: ^{1}H NMR spectra focused in the aromatic region for the supernatant of complex **2** before (top) and after the crystallization (bottom) with a focus in the aromatic region. With green box: hydroxylic proton of ethanol, red box: -CH_2 group of ester form B and blue box: -CH_3 group of ester form B.

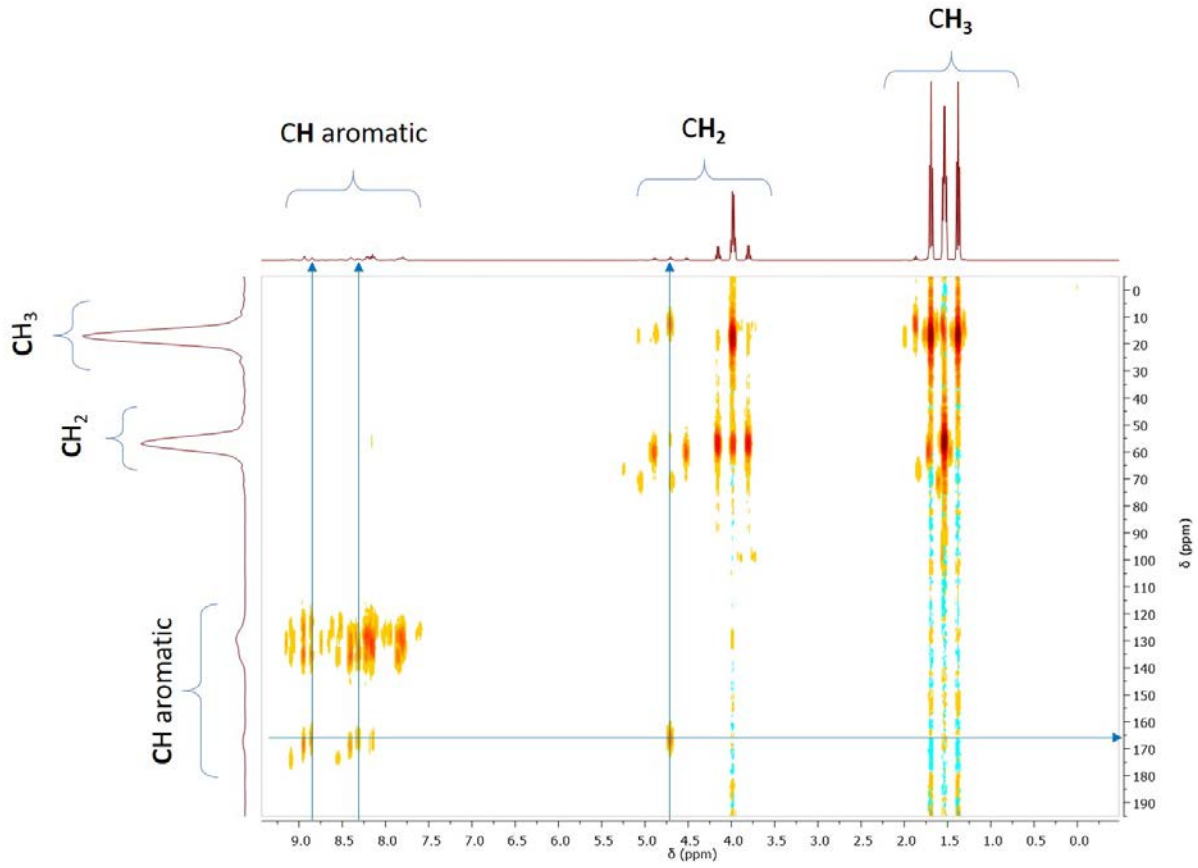


Figure 10: ^{13}C-HMBC spectrum for the supernatant of compound **2**.

The same procedure was tentatively followed for the systems **1** (involving benzoic acid) and **4** (involving 4'-methylbiphenyl-4-carboxylic acid).

The benzoic ligand in system **1** appears to be more reactive than the naphthoic ligand in system **2**. Indeed, even prior to crystallization, several intense signals are already visible on the ^{1}H NMR spectrum. These signals are quite different and much less resolved than the free ligand spectrum in $CDCl_3$ (Figure S4c). In the aromatic region, three main signals (P1, P2 and P3) centered at 7.53 ppm, 8.26 ppm and 8.35 ppm, respectively, are visible and two very small signals (P4 and P5) centered at 8.55 ppm and 8.1 ppm are present, respectively. In the aliphatic region, several peaks (labelled E1 to E4) centered at 4.22 ppm, 4.60 ppm, 4.75 ppm, 4.36 ppm respectively, and corresponding to -CH_2- groups of esters compounds are observed. It is difficult to assign these signals to the molecules occurring in the supernatant. To get more informations on the size of the various components of the mixture and based on our interpretation on the diffusion values, we have performed a DOSY measurement (Figure S4e). The E1 signal possesses a high diffusion value (compared to other systems; see Figure S4f) indicating that it is a small molecule and could therefore be interpreted as being an ethanol or ethanolate molecule. It is more probably assign to a species in equilibrium between these two forms causing the broadening of the E1 signal. This ethanol/ethanolate moiety comes from the niobium ethoxide precursor after the first complexation by a benzoic acid ligand. The acid ligand exchanges his proton with the ethanolate to form the ethanol and consequently, the benzoate ligand starts to complex the niobium centers. DOSY experiments also show that the E2 and E3 signals correspond to bigger molecules in solution, probably the unreacted niobium

ethoxide precursor or benzoate ligand coordinated to the niobium centers. P4 and E3 signals diffuse at the same speed on the DOSY spectrum (Figure S4e). Diffusion values of the P2, P3 and P1 signals suggest that the associated molecules are relatively large and could correspond to benzoate ligands linked to niobium centers.
After crystallization, the signals are well defined and can be interpreted by following the same way as we found for system **2**. For the aromatic region, the signals are visible for the H1 and H5 protons of the benzoate groups. They correspond to the acid form (noted A), the ethyl ester form (noted B) and the complex form (noted C) (Figure S4g). The HMBC 2D measurement confirms that the B signals corresponds to an ethyl ester form as correlations exist between $H1_B$/$H5_B$ with the -CH_2- groups of the ethyl ester (Figure S4h). Based on the observation made with system **2**, the two remaining signals centered at 8.03 ppm and 8.14 ppm should correspond to free benzoic acid (A) and complex ligand (B), respectively.

Before crystallization in system **4**, four signals centered at 8.71 ppm, 8.16 ppm, 8.05 ppm and 7.71 ppm are assigned to H1, H2 H3 and H4, respectively, and are related to the aromatic region (Figure S4i, top). They correspond to the acid form of the ligand (4'-methylbiphenyl-4-carboxylic acid). The -CH_3 group is also present in the aliphatic region at 2.87 ppm alongside with the niobium ethoxide precursor (signals at 4.96 ppm and 1.77 ppm). After crystallization, some modifications appear in the spectrum (Figure S4i, bottom). In the aromatic region, four main doublets are visible at 8.59 ppm, 8.07 ppm, 7.94 ppm and 7.60 ppm for protons $H1_A$, $H2_A$, $H3_A$ and $H4_A$, respectively. These protons belong to the acid form (A) of the ligand. Two small doublets are also visible on each side of the $H1_A$ signal at 8.65 ppm and 8.46 ppm. The HMBC 2D measurement reveals that the doublet located at 8.46 ppm belongs to the ethyl ester form of the ligand (B) as it is correlated to the -CH_2- group (small signal located at 5.05 ppm) of the ethyl ester. Consequently, the second doublet at 8.65 ppm stands for the presence of a small amount of acid ligand complexed to the niobium centers (C) prior to crystallization.

Discussion

The systematic reaction of the niobium ethoxide precursor with different benzene-based monocarboxylic acids gave rise to the identification of eight distinct coordination complexes, with nuclearities rising from 2 to 8.
Beside the carboxylate complexation, the common feature is the occurrence of one or several μ_2-oxo groups bridging two adjacent niobium centers, which are present as one or multiple Nb-pairs in these molecular species (1 x Nb_2 (**2**-**6**), 2 x Nb_2 (**1** & **7**), 4 x Nb_2 (**8**)). Indeed, this bridging oxygen atom is not present in the initial niobium ethoxide source $Nb(OEt)_5$, but the latter is able to undergo dimerization reaction, generating a dinuclear niobium precursor. It is thus observed by liquid ^{1}H NMR (Figure S4a), the formation of dimeric species ($Nb_2(\mu_2\text{-}OEt)_2(OEt)_8$) stabilized by two bridging μ_2-ethoxy groups together with eight terminal ethoxy groups. Such a dinuclear moiety has been structurally reported for niobium alkoxides with bridging μ_2-isopropoxy[52], μ_2-methoxy[47] and μ_2-ethoxy ligands.[39] The reaction of a carboxylic acid with the $Nb_2(\mu_2\text{-}OEt)_2(OEt)_8$ unit generates dinuclear units in which one or two central bridging μ_2-OEt groups are replaced by the carboxylate arms of the aromatic ligand

(Figure 11 [A]). Indeed, one observes the complexation by one carboxylate in compounds **3** and **5**, but still a bridging μ_2-OEt group is present (as well as a μ_2-oxo group) in [Nb_2(μ_2-O)(μ_2-OEt)(*L*)$(OEt)_6$] (*L* = bidentate aryl monocarboxylate). When two carboxylate bridges occurs in the dimer , only one central μ_2-oxo group is found in compounds **2**, **4** and **6** of type [Nb_2(μ_2-O)(*L*)$_2(OEt)_6$]. The substitution of the μ_2-OEt groups by one carboxylate arm, releases ethanol molecule (coming from H exchange between R-CO_2*H* and Nb-OEt $\rightarrow$ R-CO_2-Nb and Et-O*H*) in the medium which is able to further react with free carboxylic acid through an esterification process with the in situ production of water, leading to the hydrolysis and Nb-O-Nb condensation[44] (Figure 11 [B]). This esterification reaction has been observed in the supernatant liquor by infrared spectroscopy for the crystallization of compound **1** (Figures 9, 10) and by ^{1}H NMR for compounds **1**, **2** and **4** (Figures S4g-S4m). This carboxylate complexation is relatively rapid since IR spectra clearly indicates the formation of such niobium carboxylate species in solution after 1-hour reaction. Therefore, the monocarboxylate niobium dimeric complexes **3** and **5** can be viewed as a first step of the carboxylate complexation, with one bridging μ_2-ethoxy leaving groups substituted by one bidentate carboxylato bridging group. The presence of the additional bridging μ_2-oxo group requires the withdrawal of two terminal ethoxy groups, which contributes to the release of extra ethanol molecules in the reaction medium (from H exchange between *H*$_2$O and 2 x Nb-OEt $\rightarrow$ Nb-O-Nb and 2 x Et-O*H*; (Figure 11 [B]).). The second step of the carboxylate complexation would then lead to the formation of a dinuclear species containing two carboxylate linkers, as observed in compounds **2**, **4** and **6**, with the substitution of the second bridging μ_2-OEt group by an additional carboxylate ligand (Figure 11 [C]).

Moreover, these two distinct configurations of Nb/Ligand ratio of 2/1 or 2/2 may differ from steric hindrance of the bulky aromatic molecule, as illustrated with the position of the bridging carboxylates in *ortho* or *meta* (or *para*), relative to the position of adjacent neighboring benzene ring. Thus, the *ortho* position of carboxylate group in 1-napthoate (**3**) or anthracene-9-carboxylate (**5**) ligands gives rise to the monocarboxylate niobium dimeric complexes, whereas the respective *meta* (2-napthoate; **2**) or *para* (4-methyl-biphenylmonocarboxylate; **4**) position of the carboxylate group leads to the formation to the dicarboxylate niobium dimeric complexes. However, all these coordination complexes have been synthesized directly from the mixture of the liquid phase of niobium ethoxide with a monocarboxylic acid source, with quite low yields (< 20 %$_{Nb}$). One limiting step of such reaction could be the relatively low solubility of such aromatic monocarboxylic acids in the pure niobium ethoxide solution, which may result in Nb/Ligand ratio of 2/1 or 2/2 in dinuclear cores, independently of the steric hindrance or position of the carboxylate function, of the different monocarboxylate molecules. Indeed, in the different synthesis batches, we observed some difficulties to dissolve the monocarboxylic acid. Unreacted starting ligands were often visible as crystallizing as by-product together with the niobium coordination complexes. Depending on the solubility of the carboxylic acid in niobium ethoxide, undissolved starting ligand sometimes remains on the bottom of the vial without reacting, while the ligand placed on the top that comes first in contact with niobium ethoxide is dissolved and reacts to form crystals of the present products. By mild heating (since alkoxides are reported not to be stable in great temperatures, sublimed around 100 °C,[39] we can observe the solubilization (clear solution) but not a crystallization.

In order to investigate the influence of the monocarboxylic acid concentration, we thus investigated a second series of syntheses involving the addition of alcohol solvent. When isopropanol (HO^iPr) was used in molar ratio 0.8 $Nb(OEt)_5$ /13.1 HO^iPr (volume ratio 0.2 $Nb(OEt)_5$ /1 HO^iPr), a clear solution was systematically obtained after mixing the different source reactants (niobium ethoxide, monocarboxylic acid, isopropanol). However, when using anthracene-9-carboxylic acid, we were able to isolate in such isopropanol/niobium ethoxide mixture, a second dinuclear complex (**6**) containing two carboxylate ligands instead of one in complex **5** (synthesized in pure niobium ethoxide solution). The isopropanol solvent is assumed to promote the dissolution of the poly-benzene carboxylic acid in order to enhance the carboxylate complexation. Therefore, the formation of the monocarboxylate or dicarboxylate dimeric niobium-centered complexes is not directly correlated to the steric hindrance of the organic linker in this case.

Another aspect of the production niobium carboxylate from metal alkoxide source is the occurrence of multiple nuclearities for niobium, which have been isolated in a tetranuclear core with benzoate and 2-naphtoate bidentate bridging linkers, or octanuclear core with 2-naphtaote one. With benzoic acid (compound **1**), only a tetrameric moiety is observed with four niobium centers, located at each node of square geometry, and linked to each other through μ_2-oxo groups, resulting in a $[Nb_4(\mu_2\text{-}O)_4(L)_4(OEt)_8]$ core. The benzene rings of the four bidentate carboxylate linkers are pointed along the square plane direction for two of them, and up and downward the square plane for the two others. It is interesting to observe that the in-situ generation of water from esterification process is particularly efficient with the benzoic acid, leading directly to a tetranuclear species, instead of the dinuclear one, as observed with other poly-benzene-based monocarboxylic acids (compounds **2**-**6**). Indeed, the ethyl benzoate ester is visible just after one-hour reaction in the mother liquor (see infrared analysis, figure S3a), whereas it not observed for the other aryl acids, for which ester forms are seen when crystallized phase is produced (see ^1H NMR, for the systems **2** and **4**, for instance figures S3b, S3d). In fact, a previous study has reported the occurrence of such dinuclear species containing a central μ_2-oxo group in a benzoate complex $[Nb_2Cl_6(O_2C\text{-}C_6H_5)_2O]$[23], when the niobium source was $NbCl_5$, and mixed in chloroform or carbon tetrachloride, which was then heated at 60-110°C. For the latter, the origin of the bridging oxygen atom comes from the formation of acyl chloride ($3\ R\text{-}CO_2H + 2NbCl_5 \rightarrow R\text{-}COCl + Nb_2Cl_6(O_2C\text{-}C_6H_5)_2O$), which releases one available oxo species for the Nb-O-Nb condensation. The yield of acyl chloride reaction seems to be less efficient for the generation of dinuclear unit $[Nb_2(\mu_2\text{-}O)(L)_2Cl_6]$ compared to that giving rise straightly to a higher condensed species as found in the $[Nb_4(\mu_2\text{-}O)_4(L)_4(OEt)_8]$ core. As suggested by different authors[38,44,45], the tetranuclear entity $[Nb_4(\mu_2\text{-}O)_4(L)_4(OEt)_8]$ can be viewed as the assembly of two dinuclear $[Nb_2(\mu_2\text{-}O)(L)_2(OEt)_6]$ bricks via two additional μ_2-oxo groups, coming from the removal of four terminal ethoxy groups (Figure 11 [D] and S5a). This tetrameric entity can thus be considered as a second step of condensation with the formation of additional double Nb-O-Nb linkages.

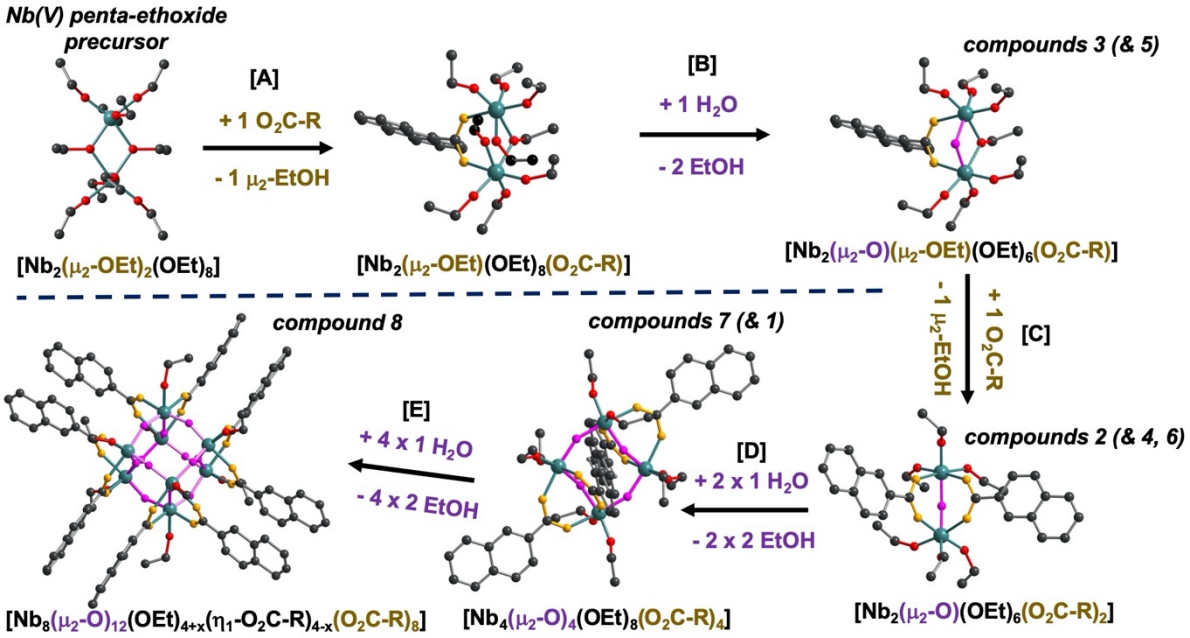


Figure 11: Schematic proposed reactional pathways for the formation of dinuclear, tetranuclear and octanuclear cores of niobium(V) monocarboxylates coordination complexes **1**-**8**. For compound **8**, only bidentate 2-naphtoate linkers are shown; terminal monodentate 2-naphtoate ligand are not shown for clarity. Green: niobium; dark grey: carbon; red: oxygen from ethoxy group; purple: bridging oxygen between Nb centers; orange: oxygen from bidentate carboxylate groups.

With benzoic acid, it was only possible to isolate either a crystalline dinuclear or tetranuclear species by changing the niobium source ($NbCl_5$ or $Nb(OEt)_5$). It seems that multiple nuclearity was not reported in literature for a given niobium precursor. Indeed, it was proposed that steric hindrance of the ligand might orientate the nuclearity of the complex as illustrated in the work of Boyle[45], for which a dimer was obtained with a bulky molecule (pivalic acid), whereas a tetramer is obtained with a less bulky molecule (terbutylacetic acid), prepared in the same synthetic conditions. In fact, by using 2-naphthoic acid, we show here that the nuclearity of the inorganic core is controlled by the hydrolysis rate. For a low water content (coming from esterification reaction at room temperature), the dinuclear core $[Nb_2(\mu_2\text{-}O)(L)_2(OEt)_6]$ (compound **2**) is observed, whereas the tetranuclear core $[Nb_4(\mu_2\text{-}O)_4(L)_4(OEt)_8]$ (compound **7**) has been identified in a closed reaction medium saturated with 55% water humidity. This suggests that an increasing water content promotes the Nb-O-Nb condensation process, which can favor the formation of higher nuclearity in niobium carboxylate complexes. The last coordination complex observed in our system involving 2-naphthoic acid, is the isolation of poly-oxo cluster containing eight niobium centers located at each node of a cubic geometry (compound **8**). Indeed, its crystal structure exhibits one octanuclear moiety which is stabilized under two slightly different forms, with a general formula of $[Nb_8(\mu_2\text{-}O)_{12}(L)_8(OEt)_{4+x}(\eta_1\text{-}L)_{4-x}]$ (x = 0 or 2), with varying numbers of terminal ethoxy/naphthoic acid groups. Apart that this octamer is new in chemistry of niobium carboxylates poly-oxo clusters, it is a good illustration of a third step for the condensation Nb-O-Nb process, by considering the association of two tetramers $[Nb_4(\mu_2\text{-}O)_4(L)_4(OEt)_8]$ through the addition of quadruple μ_2-oxo ligand between the niobium centers (Figure 11 [E]; figure S5a). For compound **8**, the hydrolysis rate is enhanced by using a solvothermal synthetic route (here heating at 100°C for 4 days in acetonitrile), which

allows for the production of higher water content through esterification increasing yield. Similar reaction conditions thus led to the synthesis of a 16-nuclearity poly-oxo cluster in $[Nb_{16}O_{28}(OEt)_{12}(piv)_{12}]$[41].

From this series, it was possible to play with the hydrolysis rate by isolating different steps of Nb-O-Nb condensation from non-oxo {Nb} species to oxo species with $\{NbO_{0.5}\}$ (compounds **2-6**), $\{NbO_{1.0}\}$ (compounds **1** & **7**), $\{NbO_{1.5}\}$ (compound **8**) and $\{NbO_{1.75}\}$[41], knowing that the ultimate member would be the infinite dense niobium oxide network $\{NbO_{2.5}\}_\infty$ as found in Nb_2O_5. It is noticeable to observe that the octanuclear $\{Nb_8O_{12}\}$ brick, as a corner-sharing octahedral arrangement of perovskite-related ReO_3 type structure, can be considered as a fragment of the Nb_2O_5 network. Although its crystal chemistry offers many complex polymorphic stackings[53], one may identify some blocks with such ReO_3 configurations, in some of them, related to different forms identified at various temperatures (Figure S5b).

The different polynuclear niobium oxo-clusters **1-8** are systematically constructed from octahedral NbO_6 polyhedra connected through a corner-sharing mode. This particular linkage fashion is surely promoted by the double bidentate carboxylate bridge, which acts as a pincer between two adjacent niobium atoms, and thus favors the oxo-corner fashion. This specific connection mode is nevertheless not observed in the chemistry of niobium-based polyoxometalates species, since the basic bricks are composed of the hexanuclear entity $[Nb_6O_{19}]^{8-}$ of Lindqvist type, or decaniobiate $[Nb_{10}O_{28}]^{6-}$, which both are characterized by edge-sharing NbO_6 octahedra.[54] These anionic moieties are able to further react to generate a large number of highly condensed oxo clusters such as the giant $\{Nb_{288}O_{768}(OH)_{48}(CO_3)_{12}\}$,[55] for instance. The edge-sharing mode is also observed in purely niobium alkoxides such as the dimeric precursors[39,47,52], hexanuclear $[Nb_6O_8(O^iPr)_{14}(HO^iPr)_2]$ species with isopropoxy groups[56] or octanuclear species $[Nb_8O_{10}(OEt)_{20}]$ with ethoxy groups.[57] Another structural difference between the niobium-based polyoxometalates and the niobium alkoxides molecules is the distinct nature of the terminal oxo groups. The polyoxometalates are usually characterized by the occurrence of terminal niobyl-oxo groups, which are not observed in the niobium mixed alkoxide-carboxylates, since the terminal oxo groups belong to alkoxo species decorating the external periphery of the polynuclear moiety.

Conclusion

In conclusion, various niobium(V)-centered cores have been identified by the use of arene or polyarene monocarboxylic acids. Indeed, by starting from the niobium ethoxide as precursor, eight different discrete molecules of niobium carboxylates poly-oxo clusters have been obtained with nuclearities varying from $\{Nb_2\}$, $\{Nb_4\}$ up to $\{Nb_8\}$, with various fashions of oxo bridges connecting the Nb centers. The synthetic condition associating carboxylic acid with leaving ethanol groups allows for the slow production of ester species with releasing water molecules, which are at the origin of the oxo-condensation bridge between the niobium centers. Indeed, the occurrence of moisture atmosphere or/and elevated temperature (up 100°C in our study) favors the generation of water molecules, which induce the formation of higher nuclearities for the resulting niobium-based poly-oxo clusters ($\{Nb_4\}$ or $\{Nb_8\}$). From the structural point of view, the addition of monocarboxylic acid to the niobium ethoxide ($Nb_2(OEt)_{10}$) led to the formation of dinuclear unit ($Nb_2O(carboxylate)_{1\text{ or }2}$), which can be assembled twice to give a tetranuclear unit ($Nb_4O_4(carboxylate)_4$). The latter can be further condensed twice again, to

produce an octanuclear brick ($(Nb_8O_{12}(carboxylate)_8)$). These different well-defined niobium(V)-centered cores can be considered as potential inorganic building units for the generation of extended networks by using polydentate carboxylic acid ligands. Indeed, from the niobium(V)-oxygen bond distance consideration, we observed that $Nb\text{-}O_{oxo}$ distances are quite shorter (≈ 1.9 Å) when compared to those observed in well-known MOF such as UiO-66 (2.23 Å)[58] for instance, but $Nb\text{-}O_{carboxylate}$ bond lengths are quite identical ($Nb\text{-}O_c$ ≈ 2.10-2.20 Å). With this purely metric view, we may expect a better chemical stability of the niobium-MOF compounds. Current works are now exploring the structural flexibility of utilizing such polynuclear units for the formation of MOF-like architectures.

Experimental Section

Reagents. The following reactants were used: niobium(V) ethoxide complex ($Nb(OCH_2CH_3)_5$, 99.95%, Sigma-Aldrich), benzoic acid ($C_7H_6O_2$, 99.5%, Sigma-Aldrich), 1-naphthoic acid ($C_{11}H_8O_2$, 96%, Sigma-Aldrich), 2-naphthoic acid ($C_{11}H_8O_2$, 98%, Sigma-Aldrich), 4'-methylbiphenyl-4-carboxylic acid ($C_{14}H_{12}O_2$, 96%, Sigma-Aldrich), anthracene-9-carboxylic acid ($C_{15}H_{10}O_2$, 99% Sigma-Aldrich), anhydrous isopropanol (C_3H_8O, HO^iPr, 99.5%, Sigma-Aldrich). The chemical reactants were commercially available, were used without any further purification and manipulated in a glove box under argon to prevent any hydrolysis reaction of the niobium(V) alkoxide into niobium(V) oxide.

Syntheses

Compound 1 $[Nb_4(\mu_2\text{-}O)_4(C_7H_5O_2)_4(OEt)_8]$: A mixture of 0.75 mL (3 mmol) $Nb(OCH_2CH_3)_5$ and 756.4 mg (6.2 mmol) benzoic acid was placed in a 2 mL glass tube, sealed with a phenolic cap, and left at room temperature. The formation of brick-like colorless crystals, was observed after one month. Compound **1** was analyzed by optical microscope showing large elongated parallelepiped-shape crystals up to 1 mm size. The resulting colorless crystals filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 24.5 $\%_{Nb}$. (Figure S1a).

Compound 2 $[Nb_2(\mu_2\text{-}O)(C_{11}H_7O_2)_2(OEt)_6]$: A mixture of 0.75 mL (3 mmol) $Nb(OCH_2CH_3)_5$ and 1.033 g (6 mmol) 2-naphthoic acid was placed in a 2 mL glass tube, sealed with a phenolic cap, and left at room temperature. Baguette-like transparent crystals appeared after 5 days. Compound **2** was analyzed by optical microscope showing large elongated parallelepiped-shape crystals up to 300 µm size. The resulting colorless crystals filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 6.1 $\%_{Nb}$. (Figure S1a).

Compound 3 $[Nb_2(\mu_2\text{-}O)(\mu_2\text{-}OEt)(C_{11}H_7O_2)(OEt)_6]$: A mixture of 0.75 mL (3 mmol) $Nb(OCH_2CH_3)_5$ and 1.033 g (6 mmol) 1-naphthoic acid was placed in a 2 mL glass tube, sealed with a phenolic cap, and left at room temperature. Baguette-like transparent crystals appeared after 6 months. Compound **3** was analyzed by optical microscope showing large elongated parallelepiped-shape crystals up to 300 µm size. The resulting colorless crystals filtered off,

washed with ethanol and dried at room temperature. Crystallization yield was 2.4 %$_{Nb}$. (Figure S1b).

Compound 4 [$Nb_2(\mu_2\text{-}O)(C_{14}H_{11}O_2)_2(OEt)_6$]: A mixture of 0.75 mL (3 mmol) $Nb(OCH_2CH_3)_5$ and 1.273 g (6 mmol) 4'-methylbiphenyl-4-carboxylic acid was placed in a 2 mL glass tube, sealed with a phenolic cap, and left at room temperature. Plate-like crystals appeared after 3 weeks. Compound **4** was analyzed by optical showing elongated parallelepiped-shape crystals up to 40 µm size. The resulting colorless crystals filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 19.1 %$_{Nb}$. (Figure S1b).

Compound 5 [$Nb_2(\mu_2\text{-}O)(\mu_2\text{-}OEt)(C_{15}H_9O_2)(OEt)_6]_2$: A mixture of 0.75 mL (3 mmol) $Nb(OCH_2CH_3)_5$ and 222.24 mg (1 mmol) anthracene-9-carboxylic acid was placed in a 2 mL glass tube, sealed with a phenolic cap, and left at room temperature. Brick-like crystals appeared after 2 weeks. Compound **5** was analyzed by optical microscope showing block-shape crystals up to 30 µm size. The resulting pale yellowish crystals filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 13.1 %$_{Nb}$. (Figure S1c).

Compound 6 [$Nb_2(\mu_2\text{-}O)(C_{15}H_9O_2)_2(O^iPr)_6$]: A mixture of 0.2 mL (0.8 mmol) $Nb(OCH_2CH_3)_5$ and 85.3 mg (0.3 mmol) anthracene-9-carboxylic acid, isopropanol 1 mL (13.1 mmol) was placed in a 2 mL glass tube, sealed with a phenolic cap, and left at room temperature. Brick-like transparent crystals appeared after 2 weeks. Compound **6** was analyzed by optical microscope showing large block-shape crystals up to 50 µm size. The resulting colorless crystals filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 4.8 %$_{Nb}$. (Figure S1c).

Compound 7 [$Nb_4(\mu_2\text{-}O)_4(C_{11}H_7O_2)_4(OEt)_8$]: A mixture of 0.2 mL (0.8 mmol) $Nb(OCH_2CH_3)_5$ and 145 mg (0.85 mmol) 2-naphthoic acid was placed in a 2 mL glass tube, sealed with a phenolic cap in inert atmosphere. The vial was placed in a desiccator with a saturated solution of Na_2CO_3 (55 % humidity) with an open cap and after 24 hours was closed and the vial was placed in the oven at 50°C. Only a powdered sample is obtained, in which needle-like transparent crystals are observed after 3 weeks. Compound **7** was analyzed by optical microscope showing large elongated parallelepiped-shape crystals up to 150 µm size. The resulting colorless crystals filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 9.7 %$_{Nb}$ (Figure S1d).

Compound 8 [$Nb_8(\mu_2\text{-}O)_{12}(C_{11}H_7O_2)_8(\eta_1\text{-}C_{11}H_7O_2)_4(OEt)_4]\cdot[Nb_8(\mu_2\text{-}O)_{12}(C_{11}H_7O_2)_8(\eta_1\text{-}C_{11}H_7O_2)_2(OEt)_6$]: A mixture of 60 µL (0.24 mmol) $Nb(OCH_2CH_3)_5$, 460 mg (2.7 mmol) 2-naphthoic acid and acetonitrile (1 mL, 19.1 mmol)) was placed in a 2 mL glass tube, sealed with a phenolic cap, and placed in an oven at 100 °C. After 4 days dark red parallelepiped blocks appeared and as the temperature decreases we observe the recrystallisation of 2-naphthoic acid and finally no supernatant is obtained. Compound **8** was analyzed by optical microscope showing large parallelepiped-shape crystals up to 40 µm size. The resulting dark red crystals filtered off,

washed with acetonitrile and dried at room temperature. Crystallization yield was 11.6 $\%_{Nb}$. (Figure S1d).
All niobium-based coordination complexes **1**-**8** were found to be stable under air for several weeks and manipulated without any specific precaution.

Single-crystal X-ray diffraction
Crystals of compounds **1**-**7** was selected under polarizing optical microscope and 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_a radiation (λ = 0.71073 Å) with an optical fiber as collimator. Several sets of narrow data frames (20s per frame for **1**, 20s for **2**, 20s for **3**, 20s for **4**, 20s for **5**, 20s for **6** and 15s for **7**) were collected at different values of q for two initial values of ϕ and ω, respectively, using 0.3° increments of ϕ with ω scans.
Due to its very small crystal size (≈ 20 x 20 x 10 μm), the X-ray diffraction intensities data of compound **8** have been collected from a Synchrotron radiation facility (PROXIMA-2A beamline, SOLEIL, France), by using a wavelength of λ = 0.774901 Å, at 100 K (under liquid nitrogen gas flow). The structural analysis shows high values for many thermal parameters, related to organic ligands. Consequently, most of the naphthoate ligands were constrained with the AFIX function (with m=11 to get idealized naphthoic groups) and Exyz constraint to get ideal aromatic rings with averages C-C distances of 1.39Å. SQUEEZE procedure implemented in the olex2 Software was used to remove residual electronic densities corresponding to disordered solvent molecules, which are too difficult to model. The procedure removed 392 electrons per cell units in the lattice.

Data reduction was accomplished using SAINT V8.34a.[59] 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.[60] 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, implemented in the OLEX2 graphical tool.[61]
The crystal data are given in Table 2. Supporting information is available in CIF format. CCDC numbers: 2172037 for **1**, 2172039 for **2**, 2172034 for **3**, 2172040 for **4**, 2172038 for **5**, 2172035 for **6**, 2172036 for **7** and 2172041 for **8** 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 2. Crystal data and structure refinements for compounds **1 - 8**.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Formula	$C_{11}H_{15}NbO_5$	$C_{34}H_{44}Nb_2O_{11}$	$C_{25}H_{42}Nb_2O_{10}$	$C_{40}H_{52}Nb_2O_{11}$	$C_{58}H_{88}Nb_4O_{20}$	$C_{192}H_{236.5}Nb_8O_{44}$	$C_{60}H_{68}Nb_4O_{20}$	$C_{262}H_{204}Nb_{16}O_{78}$
Formula weight	320.14	814.51	688.4	894.64	1476.92	3991.58	1214.54	6086.80
Temperature/K	296	102	100	100	100	100	100	100
Crystal type	colorless parallelepiped	colorless parallelepiped	colorless parallelepiped	colorless parallelepiped	colorless parallelepiped	yellowish plate	colorless needle	colorless needle
Crystal size/mm	0.20 x 0.19 x 0.13	0.99 x 0.66 x 0.30	0.58 x 0.26 x 0.10	0.13 x 0.12 x 0.11	0.31 x 0.26 x 0.13	0.28 x 0.16 x 0.10	0.42 x 0.10 x 0.09	0.02 x 0.02 x 0.01
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/c$	$P2_12_12_1$	*C*2/*c*	*P*-1	*C*2/*c*	$P2_1/c$	*C*2/*c*
a/Å	10.8589(6)	20.228(2)	8.1182(14)	25.4759(7)	11.7194(6)	21.839(2)	10.9286(10)	67.5185(14)
b/Å	11.9022(6)	8.5199(8)	19.040(3)	9.0694(3)	14.1832(7)	9.9717(11)	20.1535(15)	10.7915(2)
c/Å	12.4716(6)	20.738(2)	19.081(3)	17.9087(4)	20.3412(10)	21.376(2)	16.3901(13)	47.1089(9)
α/°	72.281(2)	90	90	90	102.816(3)	90	90	90
β/°	70.918(2)	97.487(3)	90	101.834(1)	95.187(2)	95.901(3)	120.679(3)	134.142(1)
γ°	67.815(2)	90	90	90	99.809(3)	90	90	90
Volume/Å^3	1380.08(13)	3543.5(6)	2946.4(9)	4049.9(2)	3219.6(3)	4630.6(8)	3104.7(5)	24595.5(9)
Z, $\rho_{calculated}$/g.cm^{-3}	4, 1.541	4, 1.527	4, 1.550	4, 1.467	2, 1.523	1, 1.431	2, 1.584	4, 1.644
μ/mm^{-1}	0.878	0.704	0.827	0.623	0.764	0.553	0.793	1.114
Θ range/°	1.77 - 26.40	2.11 - 30.53	1.51 - 26.42	1.63 - 26.39	1.50 - 30.53	1.92 - 26.42	1.76 - 26.39	0.92 - 25.00
Limiting indices	$-13 \le h \le 13$ $-14 \le k \le 14$ $-15 \le l \le 15$	$-28 \le h \le 28$ $-12 \le k \le 10$ $-21 \le l \le 29$	$-9 \le h \le 10$ $-23 \le k \le 22$ $-23 \le l \le 23$	$-31 \le h \le 31$ $-11 \le k \le 11$ $-22 \le l \le 19$	$-16 \le h \le 16$ $-16 \le k \le 20$ $-29 \le l \le 29$	$-27 \le h \le 27$ $-12 \le k \le 12$ $-26 \le l \le 26$	$-13 \le h \le 13$ $-23 \le k \le 25$ $-18 \le l \le 20$	$-77 \le h \le 76$ $-10 \le k \le 10$ $-55 \le l \le 55$
Collected reflections	36059	60031	20882	30431	8430	36900	24721	84196
Unique reflections	5642 [R(int) = 0.0245]	10808 [R(int) = 0.0267]	5810 [R(int) = 0.0581]	4132 [R(int) = 0.0396]	19179 [R(int) = 0.0259]	4753 [R(int) = 0.0287]	6330 [R(int) = 0.0964]	10386 [R(int) = 0.0506]
Parameters	301	466	342	254	814	303	383	1296
Goodness-of-fit on F^2	1.080	1.044	1.053	1.048	1.067	1.046	1.007	1.107
Final R indices [I>2σ(I)]	R1 = 0.0430 wR2 = 0.1193	R1 = 0.0332 wR2 = 0.0772	R1 = 0.0387 wR2 = 0.0661	R1 = 0.0272 wR2 = 0.0647	R1 = 0.0319 wR2 = 0.0780	R1 = 0.0292 wR2 = 0.0695	R1 = 0.0539 wR2 = 0.1081	R1 = 0.1008 wR2 = 0.3164
R indices (all data)	R1 = 0.0563 wR2 = 0.1364	R1 = 0.0360 wR2 = 0.0799	R1 = 0.0504 wR2 = 0.0691	R1 = 0.0366 wR2 = 0.0687	R1 = 0.0393 wR2 = 0.0820	R1 = 0.0325 wR2 = 0.07151	R1 = 0.1072 wR2 = 0.1292	R1 = 0.1280 wR2 = 0.3328
Largest diff. peak and hole/e.Å^{-3}	1.48 and -0.97	1.58 and -3.39	0.77 and -0.68	0.41 and -0.42	1.57 and -1.14	0.93 and -0.54	0.71 and -1.17	1.38 and -0.94

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 by using a classical glass specimen holder, within an angular range of 5-50° in 2θ, with steps of 0.02° and counting time of 0.5 s per step.

Infrared 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.

Liquid NMR spectroscopy

The supernatant solutions obtained after the crystallization of compounds **1**, **2** and **4** have been analyzed by solution ^{1}H-NMR at 300K and 9.4 T, on a Bruker Avance NEO 400 spectrometer equipped with a z-gradiented TBI 5 mm probe. In order to prevent any modifications by adding any substances into the samples, the solution samples have been introduced in standard 5 mm tubes with a coaxial insert (Eurisotop, Saint-Aubin, France) containing deuterated chloroform ($CDCl_3$, 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).

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Conflict of Interests
The authors declare no conflict of interest.

Data Availability Statement
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, summary of the representation of polynuclear niobium-centered cores).
Accession Codes
Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 2172037 for **1**, 2172039 for **2**, 2172034 for **3,** 2172040 for **4**, 2172038 for **5**, 2172035 for **6,** 2172036 for **7**, 2172041 for **8**. 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).

Keywords: niobium(V) ethoxide, monocarboxylic acid, coordination complex, poly-oxo clusters, single-crystal X-Ray diffraction, infrared spectroscopy, liquid ^{1}H NMR.

References

[1] T. Devic, C. Serre, *Chem. Soc. Rev.* **2014**, *43*, 6097–6115.

[2] T. Loiseau, I. Mihalcea, N. Henry, C. Volkringer, *Coord. Chem. Rev.* **2014**, *266–267*, 69–109.

[3] M. D. Korzyński, Luca Braglia, Elisa Borfecchia, K. A. Lomachenko, Amgalanbaatar Baldansuren, C. H. Hendon, Carlo Lamberti, Mircea Dincă, *Chem. Sci.* **2019**, *10*, 5906–5910.

[4] M. A. Syzgantseva, C. P. Ireland, F. M. Ebrahim, B. Smit, O. A. Syzgantseva, *J. Am. Chem. Soc.* **2019**, *141*, 6271–6278.

[5] S. Ahn, N. E. Thornburg, Z. Li, T. C. Wang, L. C. Gallington, K. W. Chapman, J. M. Notestein, J. T. Hupp, O. K. Farha, *Inorg. Chem.* **2016**, *55*, 11954–11961.

[6] M. Rivera-Torrente, C. Hernández Mejía, T. Hartman, K. P. de Jong, B. M. Weckhuysen, *Catal. Lett. 2019 14912* **2019**, *149*, 3279–3286.

[7] A. Cadiau, K. Adil, P. M. Bhatt, Y. Belmabkhout, M. Eddaoudi, *Science (80-.).* **2016**, *353*, 137–140.

[8] M. E. Ziebel, J. C. Ondry, J. R. Long, *Chem. Sci.* **2020**, *11*, 6690.

[9] N. Galešić, N. Brničević, B. Matković, M. Herceg, B. Zelenko, M. Šljukić, B. Prelesnik, R. Herak, *J. Less-Common Met.* **1977**, *51*, 259–270.

[10] L. Eriksson, G. Svensson, V. Tabachenko, J. Sjöblom, T. K. Thorsen, P. Coppens, O. Buchardt, *Acta Chem. Scand.* **1993**, *47*, 1038–1040.

[11] B. Kojić-Prodić, R. Liminga, S. Šćavaničar, IUCr, *urn:issn:0567-7408* **1973**, *29*, 864–869.

[12] G. Mathern, R. Weiss, *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* **1971**, *27*, 1610–1618.

[13] M. Šestan, B. Perić, G. Giester, P. Planinić, N. Brničević, *Struct. Chem.* **2005**, *16*, 409–414.

[14] A. A. Shmakova, E. M. Glebov, V. V. Korolev, D. V. Stass, E. Benassi, P. A. Abramov, M. N. Sokolov, *Dalt. Trans.* **2018**, *47*, 2247–2255.

[15] M. Jurić, P. Planinić, N. Brničević, D. Matković-Čalogović, *J. Mol. Struct.* **2008**, *888*, 266–276.

[16] W. X. C. Oliveira, C. L. M. Pereira, C. B. Pinheiro, K. Krambrock, T. Grancha, N. Moliner, F. Lloret, M. Julve, *Polyhedron* **2016**, *117*, 710–717.

[17] M. Jurić, B. Perić, N. Brničević, P. Planinić, D. Pajić, K. Zadro, G. Giester, B. Kaitner, *Dalt. Trans.* **2008**, 742–754.

[18] C. N. Muniz, H. Patel, D. B. Fast, L. E. S. Rohwer, E. W. Reinheimer, M. Dolgos, M. W. Graham, M. Nyman, *J. Solid State Chem.* **2018**, *259*, 48–56.

[19] M. Jurić, J. Popović, A. Šantić, K. Molčanov, N. Brničević, P. Planinić, *Inorg. Chem.* **2013**, *52*, 1832–1842.

[20] D. Bayot, B. Tinant, M. Devillers, *Catal. Today* **2003**, *78*, 439–447.

[21] D. Bayot, B. Tinant, B. Mathieu, J.-P. Declercq, M. Devillers, *Eur. J. Inorg. Chem.* **2003**, *2003*, 737–743.

[22] D. Bayot, A. Bernard Tinant, M. Devillers, *Inorg. Chem.* **2005**, *44*, 1554–1562.

[23] D. A. Brown, M. G. H. Wallbridge, N. W. Alcock, *J. Chem. Soc. Dalt. Trans.* **1993**, 2037–2039.

[24] D. A. Brown, M. G. H. Wallbridge, W. S. Li, M. McPartlin, I. J. Scowen, *Inorganica Chim. Acta* **1994**, *227*, 99–104.

[25] D. A. Brown, M. G. H. Wallbridge, W. S. Li, M. McPartlin, *Polyhedron* **1994**, *13*, 2265–2270.

[26] D. A. Brown, M. G. H. Wallbridge, N. W. Alcock, *J. Chem. Soc., Dalt. Trans.* **1993**,

2037–2039.
[27] D. C. Bradley, R. C. Mehrotra, I. P. Rothwell, A. Singh, in *Alkoxo Aryloxo Deriv. Met.* (Eds.: D.C. Bradley, R.C. Mehrotra, I.P. Rothwell, A. Singh), Academic Press, London, **2001**, pp. 383–443.
[28] D. C. Bradley, *Chem. Rev.* **1989**, *89*, 1317–1322.
[29] D. C. Bradley, R. C. Mehrotra, D. P. Gaur, *Metal Alkoxides*, Academic Press, United Kingdom, **1978**.
[30] C. D. Chandler, C. Roger, M. J. Hampden-Smith, *Chem. Rev.* **1993**, *93*, 1205–1241.
[31] I. Gautier-Luneau, A. Mosset, J. Galy, *Zeitschrift für Krist. - Cryst. Mater.* **1987**, *180*, 83–96.
[32] S. Doeuff, Y. Dromzee, F. Taulelle, C. Sanchez, *Inorg. Chem.* **1989**, *28*, 4439–4445.
[33] T. J. Boyle, R. P. Tyner, T. M. Alam, B. L. Scott, J. W. Ziller, B. G. Potter, *J. Am. Chem. Soc.* **1999**, *121*, 12104–12112.
[34] T. J. Boyle, T. M. Alam, C. J. Tafoya, B. L. Scott, *Inorg. Chem.* **1998**, *37*, 5588–5594.
[35] U. Schubert, E. Arpac, W. Glaubitt, A. Helmerich, C. Chau, *Chem. Mater.* **1992**, *4*, 291–295.
[36] D. J. Eichorst, K. E. Howard, D. A. Payne, S. R. Wilson, *Inorg. Chem.* **1990**, *29*, 1458–1459.
[37] N. Steunou, C. Bonhomme, C. Sanchez, J. Vaissermann, L. G. Hubert-Pfalzgraf, *Inorg. Chem.* **1998**, *37*, 901–910.
[38] L. G. Hubert-Pfalzgraf, V. Abada, S. Halut, J. Roziere, *Polyhedron* **1997**, *16*, 581–585.
[39] T. J. Boyle, T. M. Alam, D. Dimos, G. J. Moore, C. D. Buchheit, H. N. Al-shareef, E. R. Mechenbier, B. R. Bear, J. W. Ziller, **1997**, *2*, 3187–3198.
[40] J. H. T. and, K. H. Whitmire*, *Inorg. Chem.* **2003**, *42*, 2014–2023.
[41] M. D. Korzyński, L. S. Xie, M. Dincă, *Helv. Chim. Acta* **2020**, *103*, e2000186.
[42] A. K. Narula, B. Singh, P. N. Kapoor, R. N. Kapoor, *Transit. Met. Chem.* **1983**, *8*, 195–198.
[43] N. E. Brese, M. O'Keeffe, IUCr, *urn:issn:0108-7681* **1991**, *47*, 192–197.
[44] N. Steunou, C. Bonhomme, C. Sanchez, J. Vaissermann, L. G. Hubert-Pfalzgraf, *Inorg. Chem.* **1998**, *37*, 901–910.
[45] T. J. Boyle, N. L. Andrews, T. M. Alam, M. A. Rodriguez, J. M. Santana, B. L. Scott, *Polyhedron* **2002**, *21*, 2333–2345.
[46] A. A. Pinkerton, D. Schwarzenbach, L. G. Hubert-Pfalzgraf, J. G. Riess, *Inorg. Chem.* **2002**, *15*, 1196–1199.
[47] G. G. Nunes, G. A. Seisenbaeva, V. G. Kessler, *J. Sol-Gel Sci. Technol. 2007 431* **2007**, *43*, 105–109.
[48] F. Laves, W. Petter, H. Wulf, F. Laves, W. Petter, H. Wulf, *NW* **1964**, *51*, 633–634.
[49] P. B. Arimondo, F. Calderazzo, R. Hiemeyer, C. Maichle-Mössmer, F. Marchetti, G. Pampaloni, J. Strähle, *Inorg. Chem.* **1998**, *37*, 5507–5511.
[50] Y. Cai, S. Yang, S. Jin, H. Yang, G. Hou, J. Xia, *J. Cent. South Univ. Technol. 2011 181* **2011**, *18*, 73–77.
[51] C. Djordjević, V. Katović, *J. Inorg. Nucl. Chem.* **1963**, *25*, 1099–1109.
[52] E. P. Turevskaya, N. Y. Turova, A. V. Korolev, A. I. Yanovsky, Y. T. Struchkov, *Polyhedron* **1995**, *14*, 1531–1542.
[53] L. A. Reznichenko, V. V. Akhnazarova, L. A. Shilkina, O. N. Razumovskaya, S. I. Dudkina, *Crystallogr. Reports 2009 543* **2009**, *54*, 483–491.
[54] J. Dopta, L. K. Mahnke, W. Bensch, *CrystEngComm* **2020**, *22*, 3254–3268.
[55] Y. L. Wu, X. X. Li, Y. J. Qi, H. Yu, L. Jin, S. T. Zheng, *Angew. Chemie - Int. Ed.* **2018**, *57*, 8572–8576.
[56] G. A. Seisenbaeva, A. I. Baranov, P. A. Shcheglov, V. G. Kessler, *Inorganica Chim.*

Acta **2004**, *357*, 468–474.
[57] D. C. Bradley, M. B. Hursthouse, P. F. Rodesiler, *Chem. Commun.* **1968**, 1112–1113.
[58] J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, *J. Am. Chem. Soc.* **2008**, *130*, 13850–13851.
[59] SAINT Plus Version 7.53a, *Bruker Anal. X-ray Syst. Madison, WI*, **2008**.
[60] L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* **2015**, *48*, 3–10.
[61] G. M. Sheldrick, *Acta Crystallogr. Sect. C, Struct. Chem.* **2015**, *71*, 3–8.