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Polynuclear Tantalum(V) Coordination Complexes. From dinuclear $\{Ta_8O_{12}\}$ oxo species connected through aryl monotopic carboxylate linkers

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ABSTRACT: A series of monocarboxylic ligands (benzoic acid, 1-naphtoic acid, 2-naphtoic de Online acid, antracene-9-carboxylic acid and 4'-methylbiphenyl-4-carboxylic acid) has been used to react upon mild heating with the pentavalent ethoxide tantalum(V) precursor Ta(OEt)₅ in isopropanol solvent. Five new molecular coordination compounds were isolated from crystallization upon cooling of the reactant's mixtures at room temperature. The different systems crystallized under dimeric {Ta₂O} (compound 1 and 2), tetrameric {Ta₄O₄} (compound 3 and 4) or octameric {Ta₈O₁₂} (compound 5) metal-oxo units stabilized by a combination of monocarboxylic ligands and isopropanolate solvent molecules. The five molecular samples were characterized in solid state by single-crystal and powder X-ray diffraction analyses, infrared spectroscopy, scanning electron microscopy (SEM) and thermogravimetric (TG) analysis. The chemical properties of the compounds 1 & 5 have been tested for the catalytic conversion of dihydroxyacetone, showing a Brønsted acidity.

Keywords: tantalum(V), polynuclear compounds, carboxylic acid, coordination complex, single-crystal X-ray diffraction.

Introduction

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Tantalum and niobium are known to be two closely related transition metals belonging to the same column (group 5) of the periodic table and attracted a lot of attention in past decades owing to the acidic catalytic properties in different fields of applications, the used materials are usually inorganic such as oxides, hydroxides, phosphates or MOFs.¹ They have gained significant attention in molecular chemistry due to their ability to form a wide variety of stable oxo-clusters. When decorated with organic ligands at the molecular level, they may exhibit tunable chemical properties that make them versatile in the construction of complex molecular architectures with various nuclearities ranging from dimers to hexadecamers for niobium and dimers to octanuclear species with tantalum.^{2,3} The organic ligands attached to the metal-oxo clusters play a crucial role in modulating the properties of these complexes and may influence solubility, stability and reactivity. Following previous work done in our laboratory with niobium(IV and V) cation,^{4–7} this work is focused on the coordination potentialities of the tantalum(V) cation with monocarboxylate linkers in the formation of polynuclear metal-oxo clusters.

Surprisingly, with tantalum, relatively few examples of such molecular compounds have been described in the literature and they can be regrouped in two different categories. Indeed, these compounds are either full tantalum-oxo clusters or fall in the domain of organometallic chemistry with precursors possessing one or several tantalum-carbon bonds that are further used for coordination by oxo-donor ligands on the remaining free positions of the cationic centers. Most of the literature on organometallic tantalum compounds described the use of the well-known cyclopentadienyl Cp* ligand to form [Cp*TaCl₄] precursors. The Cp* hinders one face of the tantalum cation and the remaining labile chloride atoms can then be completely or partially substituted by various oxo-, N-, or C- donors ligands to form mainly mononuclear compounds^{8–19}. Following this route, some polynuclear entities were also obtained with the

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identification of the tri- and tetra-nuclear molecules $[{TaCp*(OH)(OH_2)}_3(\mu_{1:10:1059}^3, \mu_{1:10:1059}^3, \mu_{1:10:1059}$

Albeit being studied since several decades, these compounds do not present many applications other than acting as C=O bond activators or as polymerization catalysts for methyl methacrylate synthesis.^{13,19} Few other examples were also reported using N-heterocyclic carbene as ligand for tantalum complexation with catalytic properties for cyclic carbonates formation^{23,24} or incorporation of carbon based electrophile to form metal alkyl substract or various compounds by additional reaction of the tantalum complex.²⁵ It is worth mentioning that for catalytic purpose, some tantalum hydride compounds were also described and used for carbon dioxide reduction reactions.^{26,27} From a fundamental point of view, tantalum compounds presenting an unique coordination mode of dinitrogen was also described and further used for to react with propene or bromobenzyl.²⁸

In the approach based on classical coordination chemistry using oxo-donor ligands such as alkoxides or carboxylates, several molecular compounds were previously described by other research groups, sometimes with the addition of other hetero-ligands. Although the synthetic strategies and composition may diverge, the resulting products that were reported are constructed around oxo-tantalum species with nuclearities going from a simple cation to octanuclear oxo-clusters. For tantalum(V), most of the results turn around the synthesis of single tantalum complexes that were used for lots of applications. One may mention their use for Nb^V/Ta^V separations,²⁹ the use of halide [MX₅] compounds (M = Nb^V, Ta^V) for anhydride C-H activation reactions³⁰, deposition of thin film of Ta₂O₅ using the complex [Ta(NMe₂)₄(dmbl)] (dmbl = diterbutylmalonato)³¹ and, in a more fundamental approach, discovering the coordination potentialities of the Ta(V) cation. ^{32–38}

Several mixed-metals compounds associating tantalum were obtained using oxalate $(C_2O_4)^{2-}$ or salicylate $(O_2C-C_6H_4-2-OH)^-$ ligands. In these systems, the additive metallic cation (Bi, Ni) is either directly incorporated in the polynuclear core to form {BiTa₄O₄}, {Bi₂Ta₂O} oxocluster^{39–41} or stand as an hybrid counter cation of [ML₃]ⁿ⁺ type (with L = phenanthroline or bipyridine) compensating the negative charge of [TaO(C₂O₄)]³⁻ complexes in the work of Dubraja *et al.*^{42–46}

The literature related to the topic we develop and describe in the present contribution appears relatively sparse compared to the work presented above. Only a few examples of polynuclear tantalum-oxo species were described using only oxo-donor ligands. In these results, tantalum was isolated possessing various nuclearities with, for example, several dinuclear $\{Ta_2O\}$ and tetranuclear $\{Ta_4O_4\}$ moieties and a few octanuclear $\{Ta_8O_{12}\}$ cores. Most of the reactions described in the literature were performed starting from non-common precursors such as the mixed chloride-dimethylsulfide $[Ta_2Cl_6(SMe_2)_3]$ and the tetraperoxo-guanidinium tantalum $[(gu)_3Ta(O_2)_4]$ or the more classical pentachloro tantalum $TaCl_5$. They gave rise to the isolation of dimeric entities with various carboxylate ligands, for instance $\{Ta_2Cl_8(p-Cl-benz)\}$ with p-Cl-benz = p-chlorobenzoate⁴⁹ and $\{Ta_2(lactate)_4(O_2)_2O\}$ with lactate ⁵⁰ or with some other ligands.^{51,52}

Tetranuclear species like $\{Ta_4(\mu-O)_4(\mu-OBc)_4(ONep)_8\}^{52}$ or $\{Ta_4(\mu-O)_4Cl_8(p-Mebenzoate)_4\}^{53}$ were also synthetized using more bulky carboxylate ligands (OBc = pivalate and *p*-Mebenzoate) = para-methylbenzoate), eventually associated with alkoxyde molecules (ONep = 2,2-

dimethylpropan-1-olate) using standard solution synthesis. In these cases, the bulky nature of the Online bulk in the ligands was reported as being the main driving force of the increase in nuclearity of the tantalum-oxo core. Another tetranuclear compounds with applications in ring opening polymerization was described using the bifunctional (carboxylate and alcoholate) benzylic acid ligand.⁵¹

Finally, in the race to obtain large clusters, the first octanuclear tantalum compound $\{Ta_8(\mu - O)_{12}(O_2CNEt_2)_{16}\}$ ($O_2CNEt_2 =$ diethyl carbamate) was structurally characterized by Pampaloni et. Al in 1998. It remain the only illustration in tantalum "hybrid" chemistry up to date.³

Herein we report on new results obtained by using five aromatic monocarboxylic acid ligands to investigate their reactivity towards tantalum penta-ethoxide Ta(OEt)₅ precursor as the tantalum(V) metal source and generating diverse Ta-centered nuclearities. Anthracene-9-carboxylic acid and 4'-methylbyphenyl-4-carboxylic acids (dimeric compounds 1 and 2), benzoic acid and 1-naphtoic acid (tetrameric compounds 3 and 4) and 2-naphtoic acid (octameric compound 5) were successfully used to form crystalline materials. A solvent approach was successfully used to ensure high crystalline yield of the octanuclear core 5. All molecules were further analyzed by a combination of solid-state analyses (single crystal and powder X-ray diffraction, IR spectroscopy, TGA, optical binocular and SEM images). The acidity of the crystallized compounds 1 and 5 was tested for the conversion of hydroxyacetone (DHA) in water.

Experimental Section

Reagents. The following reactants were used: tantalum (V) ethoxide complex (Ta(OEt)₅, 99%, Thermo Fisher), benzoic acid ($C_7H_6O_2$, 99.5%, Sigma Aldrich), 1-naphtoic acid ($C_{11}H_8O_2$, 96%, Sigma Aldrich), 2-napthoic acid ($C_7H_6O_2$, 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 , 99.5%, Sigma Aldrich), anhydrous acetonitrile (C_4H_3N , 99.8%, Thermo Fisher). The chemical reactants were commercially available, were used without any further purification.

Syntheses

The water-sensitive tantalum(V) alkoxide precursor was used and manipulated in a glove box under argon to prevent any hydrolysis reaction of the tantalum(V) alkoxide into tantalum(V) oxide. Due to the high sensitivity of the tantalum ethoxide precursor in regard of moisture, all synthesis mixtures were prepared under a glovebox using dried solids and extra dried isopropanol (iPrOH) or acetonitrile (CH₃CN) solvents. The dry solvents were purchased and used without any additional drying. After heating, the vials were removed from the oven and left to fast cooling at room temperature. After reaction, all the synthesis batches give rise to the identification of five crystalline materials with single crystal solids of sufficient quality (Figure S1) for performing single crystal X-ray diffraction (SC-XRD) analyses.

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Compound 1 [(Ta₂(μ -O)(OiPr)₆)(C₁₅H₉O₂)₂]. A mixture of 3.5 μ L (0.013 mmol) Ta(CiPC)ticle Online and 8.9 mg (0.040 mmol) of anthracene-9-carboxylic acid was placed in a 2 mL glass tube, sealed with a phenolic cap. The vial was heated at 100°C for 5 days in an oven. Block transparent crystals appeared after 3 days upon cooling (Figure S1). Compound 1 was analyzed by optical and scanning electron microscope showing large plate-shaped crystals up to 300 μ m size. The resulting crystals were filtered off, washed with ethanol and dried at room

temperature. Crystallization yield was 88.3 %_{Ta}.

Elemental analyses: C (49.1 %), H (5.1 %). Calc. C (51.1 %), H (5.6 %).

Compound 2 [(Ta₂(μ -O)(OiPr)₆)(C₁₄H₁₁O₂)₂]. A mixture of 3.5 μ L (0.013 mmol) Ta(OEt)₅ and 8.4 mg (0.040 mmol) of 4'-methylbiphenyl-4-carboxylic acid was placed in a 2 mL glass tube, sealed with a phenolic cap. The vial was heated at 100°C for 5 days in an oven. Block transparent crystals appeared after 5 weeks upon cooling (Figure S1). Compound 2 was analyzed by optical microscope showing parallelepiped-shape crystals up to 150 μ m size. The resulting crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 12.8 %_{Ta}.

Compound 3 [(Ta₄(μ -O)₄(OiPr)₈(C₇H₅O₂)₄]. A mixture of 3.5 μ L (0.013 mmol) Ta(OEt)₅ and 4.9 mg (0.040 mmol) of benzoic acid was placed in a 2 mL glass tube, sealed with a phenolic cap. The vial was heated at 100°C for 5 days in an oven. block transparent crystals appeared after 6 weeks (Figure S1). Compound **3** was analyzed by optical and microscope showing plate-shaped crystals up to 400 μ m size. The resulting yellowish crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 17.3 %_{Ta}. Elemental analyses: C (35.2 %), H (4.2 %). Calc. C (35.8 %), H (4.36 %).

Compound 4 [(Ta₄(\mu-O)₄(OiPr)₈(C₁₁H₇O₂)₄]. A mixture of 3.5 μ L (0.013 mmol) Ta(OEt)₅ and 6.9 mg (0.040 mmol) of 1-naphtoic acid was placed in a 2 mL glass tube, sealed with a phenolic cap. The vial was heated at 100°C for 5 days in an oven. Block transparent crystals appeared after 1 day (Figure S1). Compound 4 was analyzed by optical and microscope showing square block crystals up to 150 μ m size. The resulting yellowish crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 68.3 %_{Ta}. Elemental analyses: C (42.2 %), H (4.2 %). Calc. C (42.0 %), H (4.3 %).

Compound 5 [(Ta₈(μ -O)₁₂(OiPr)₈)(C₁₁H₇O₂)₈]. A mixture of 3.5 μ L (0.013 mmol) Ta(OEt)₅ and 6.9 mg (0.040 mmol) of 2-naphtoic acid was placed in a 2 mL glass tube, sealed with a phenolic cap. The vial was heated at 100°C for 5 days in an oven. Rectangle transparent crystals appeared after 3 days (Figure S1). Compound 5 was analyzed by optical and microscope showing parallelepipedal crystals up to 400 μ m size. The resulting yellowish crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 75.3 $%_{0Ta}$.

Elemental analyses: C (38.3 %), H (3.04 %). Calc. C (38.6 %), H (3.2 %).

For analytical purpose, all the synthesis can be performed in higher quantity using $12 \text{ mL}^{\text{Visvial ticle Online}}$ increasing the precursors and solvent amount by five. The purity of the compounds 1-5 phases was confirmed using powder X-ray diffraction analyses. Only compound 2 was systematically obtained with probably unreacted ligands as can be seen on the IR spectroscopy section were a $v_{C=O}$ vibration is still observed at 1687 cm⁻¹ after reaction in the compound mixture preventing the elemental analyses.

Single-crystal X-ray diffraction

Crystals of compounds 1-5 were selected under polarizing optical microscope and all crystals were mounted on MicroMount patented by MiTeGen, inserted into a goniometer base to perform single-crystal X-ray diffraction experiment. X-ray intensity data were collected on a Bruker DUO-APEX2 diffractometer using Mo- K_{α} ($\lambda = 0.71073$ Å) or Ag- K_{α} ($\lambda = 0.56086$ Å) radiations with an optical fiber as collimator. Several sets of narrow data frames (10s per frame) were collected at different values of θ for two initial values of ϕ and ω , respectively, using 0.3° increments of ϕ with ω scans.

Data reduction was accomplished using SAINT V8.34a.⁵⁴ 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.⁵⁵ The structures were solved by direct methods, developed by successive difference Fourier syntheses, and refined by full-matrix least-squares on all F² data using SHELX program suites,⁵⁶ implemented in the OLEX2 graphical tool.⁵⁷

The crystal data are given in Table 1. Supporting information is available in CIF format. CCDC numbers: 2446460 for 1, 2446461 for 2, 2446462 for 3, 2446463 for 4 and 2446464 for 5 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.

Catalytic reaction

1,3-dihydroxyacetone dimer, >97%, purchased from Sigma-Aldrich was used to prepare 0.1 M solution in deionized water. 20 ml of this solution was placed into a glass tube (Radleys carousel) containing 150 mg of catalyst. The reaction was conducted at a temperature of 90°C with continuous stirring at 400 rpm for 6 h. Samples were taken with a 1 mL syringe through the septum and analysed by high-performance liquid chromatography (HPLC) (Model Shimadzu Prominence) with a refractive index detector (RID) equipped with a COROGEL 107H column at 40 °C to quantify the products and the residual substrate, and acidified water (H₂SO₄ 1.7mM) was used as mobile phase (0.6 mL.min⁻¹). Upon the completion of the reaction, the resultant solutions were subjected to centrifugation (10,000 rpm, 15 min) to facilitate the separation of the catalyst from the solution.

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	1	2	3	4	5
Formula	C ₄₈ H ₆₀ Ta ₂ O ₁₁	C ₄₆ H ₆₄ Ta ₂ O ₁₁	C ₅₂ H ₇₆ Ta ₄ O ₂₀	C ₆₈ H ₂₄ Ta ₄ O ₂₀	C ₁₁₂ H ₁₁₀ Ta ₈ O ₃₆
Formula weight	1174.86	1154.87	1744.92	1945.15	6961.23
Temperature/K	296	100	296	296	296
Crystal type	colorless plate	colorless block	colorless block	colorless block	colorless block
Crystal size/mm	0.15 x 0.12 x	0.227 x 0.086 x	0.121 x 0.118 x	0.206 x 0.085 x	0.27 x 0.13 x 0.12
	0.02	0.075	0.087	0.078	
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	C2/c	C2/c	$P2_1/n$	$P2_1/n$	<i>P</i> -1
a/Å	22.0631(12)	24.6357(5)	11.9823(9)	14.4485(8)	11.3938(14)
b/Å	10.1086(4)	9.2183(2)	18.5216(15)	12.6909(7)	23.187(4)
c/Å	21.7781(11)	21.2142(5)	14.4260(12)	20.2649(10)	24.311(4)
$\alpha/^{\circ}$	90	90	90	90	87.046(5)
$\beta/^{\circ}$	95.399(2)	94.4971(9)	95.784(3)	102.8516(16)	78.852(5)
γ°	90	90	90	90	80.786(5)
Volume/Å ³	4835.6(4)	4802.90(18)	3185.3(4)	3622.8(3)	6218.8(17)
Z, $\rho_{calculated}/g.cm^{-1}$	4, 1.614	4, 1.597	2, 1.819	2, 1.783	1, 1.859
3					
μ/mm^{-1}	2.465	4.608	3.717	3.275	3.806
Θ range/°	2.711 - 20.551	1.926 - 26.382	2.065 - 23.638	2.526 - 21.982	0.674 - 20.702
Limiting indices	$-27 \le h \le 27$	$-30 \le h \le 30$	$-17 \le h \le 16$	$-19 \le h \le 19$	$-13 \le h \le 14$
	$-12 \le k \le 12$	$-11 \le k \le 11$	$-26 \le k \le 26$	$-16 \le k \le 16$	$-29 \le k \le 29$
	$-27 \le l \le 27$	$-26 \le l \le 26$	$-20 \le l \le 19$	$-26 \le l \le 27$	$-30 \le l \le 30$
Collected	70322	61939	100994	116530	339380
reflections					
Unique	4952	4922	9720	8972	25543
reflections	[R(int) = 0.0777]	[R(int) = 0.0496]	[R(int) = 0.0407]	[R(int) = 0.0608]	[R(int) = 0.0725]
Parameters	282	321	381	423	1343
Goodness-of-fit	1.092	1.082	1.166	1.220	1.116
on F ²					
Final R indices	R1 = 0.0281	R1 = 0.0346	R1 = 0.0262	R1 = 0.0279	R1 = 0.0766
$[I \ge 2\sigma(I)]$	wR2 = 0.0544	wR2 = 0.0661	wR2 = 0.0461	wR2 = 0.0531	wR2 = 0.1469
R indices (all	R1 = 0.0447	R1 = 0.0496	R1 = 0.0428	R1 = 0.0462	R1 = 0.1258
data)	wR2 = 0.0628	wR2 = 0.0690	wR2 = 0.0559	wR2 = 0.0635	wR2 = 0.1907
Largest diff.	1.38 and -0.89	2.34 and -2.29	1.74 and -0.82	1.57 and -0.86	7.12 and -3.448
peak and					
hole/e.Å ⁻³					

Table 1. Crystal data and structure refinements for compounds 1 - 5.

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_{α} radiation. Each powder pattern was recorded within an angular range of 5-50° in 2 θ , with steps of 0.02° and counting time of 0.5 s per step.

Scanning electron microscopy

The SEM analyses of tantalum(V) coordination complexes 1-5 were performed on a Hitachi-S3400N microscope, equipped with a tungsten filament (acceleration voltage = 5 kV, secondary electron mode, working distance = 5.3 to 5.5 mm).

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IR spectroscopy

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Infrared spectra were measured on Perkin Elmer Spectrum TwoTM spectrometer between 4000 and 400 cm⁻¹, equipped with a diamond Attenuated Total Reflectance (ATR) accessory. No ATR correction was applied on the spectrum.

Thermal behavior

Thermogravimetric analyses were performed on a thermoanalyzer 92 SETARAM TGA apparatus under an air atmosphere from room temperature up to 800°C at a rate of 5 °C.min⁻¹.

Results and discussion

Structure Description

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Single crystal X-ray diffraction was performed on the five compounds to determine their structural arrangement. From this analysis, it appears that they crystallize to form three different structural assemblies. Compounds 1 and 2, synthesized with anthracene-9-carboxylic acid and 4'-methylbiphenyl-4-carboxylic acid respectively are obtained as tantalum dimers with a $\{Ta_2O\}$ core, compounds 3 and 4 with benzoic acid and 1-naphtoic acid crystallize as tetramers with $\{Ta_4O_4\}$ moieties and compound 5 with 2-naphtoic acid is obtained as an octamer with a $\{Ta_8O_{12}\}$ core.

Compounds 1 and 2 of the general formula type $[Ta_2(\mu^2-O)(L)_2(OiPr)_6]$

The two first compounds crystallize in a monoclinic C2/c space group with close cell parameters (See Table 1) and can be described the same way. The only difference lies in the change of the ligand used for the complexation of the tantalum centers. In both molecules, the asymmetric unit in the crystal structure is constructed by the one independent tantalum center (Ta1), one monotopic ligand, three isopropanolate ligands coming from the solvent used in the synthesis and one oxygen atom bridging the two tantalum centers in the complete molecular architecture. The molecular system is a neutral compound composed of a dimeric $\{Ta_2O\}$ moieties surrounded by a total of two carboxylate and six isopropanolate ligands (Figure 1). Each tantalum center is six-fold coordinated with a distorted octahedral geometry in an oxygen environment. It is linked by three oxo groups from isopropanolate molecules, with Ta-O_iPr bond distances varying from 1.859(4) Å to 1.877(3) Å for compound 1, and from 1.863(4) Å to 1.900(4) Å for compound 2; two oxo groups from carboxylate arms (Ta-O = 2.163(3) Å and Ta-O = 2.207(3) Å) for compound 1 and (Ta-O = 2.146(3) Å and Ta-O = 2.178(3) Å) for compound 2. Finally, the coordination sphere of both tantalum atoms is completed by one oxygen atom bridging the two centers together with Ta-O distances of 1.9133(12) Å for compound 1 and 1.9221(14) Å for the compound 2. The Ta1-Ta1 distances in the molecular entity are about 3.657 Å and 3.677 Å for compounds 1 and 2, respectively. Interestingly, the two carboxylate functions from two distinct monotopic ligands (either anthracene-9carboxylate or 4'-methylbiphenyl-4-carboxylate) linked two adjacent tantalum centers, in a syn-syn bidentate bridging fashion, adopting a cis position and causing a distortion of the dimeric $\{Ta_2O\}$ unit with a Ta1-O1-Ta1 angle of about 145.7°.

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Figure 1. Structural representation of compound 1 and 2; (a) side view showing the "syn-syn" bridging coordination mode and (b) top view illustrating the "cis" coordination of both carboxylate ligands.

Compounds 3 and 4 of the general formula type $[Ta_4(\mu^2-O)_4(L)_4(OiPr)_8]$

Both compounds crystalize in the monoclinic $P2_1/n$ space group with different cell parameters (See Table 1). They can be both described as a neutral tetranuclear tantalum(V)-centered ${Ta_4O_4}$ motif stabilized either by benzoate or 1-naphtoate ligands and further decorated by eight isopropanolate groups (Figure 2). It is built up from two crystallographically inequivalent tantalum(V) atoms, Ta1 and Ta2, linked to each other via μ^2 -oxo groups, within a square-ring unit (Figure 2). Conceptually, these tetranuclear blocks can be seen as the association of two dinuclear subunits as the one described for compounds 1 and 2 through the addition of two bridging μ^2 -oxo groups. It is worth noting that in this association, the two dimers are connected together in a sort of "head-tail" mode where two ligands are on the same plane and the two others are located above and under this plane (See Figure 2b). Each tantalum centers of complexes 3 and 4 are in a six-fold coordination oxo environment with a distorted octahedral geometry. The tantalum cations are surrounded by two μ^2 -oxo groups with Ta-O distances comprised between 1.896(2) Å and 1.928(2) Å for compound **3** and between 1.896(3) Å and 1.939(3) Å in compound 4. Two oxygen atoms belong to isopropanolate groups and are bound to the tantalum with distances ranging from 1.863(3) Å to 1.899(2) Å for compound 3 and from 1.875(3) Å to 1.885(3) Å for compound 4. The coordination sphere is completed by the two carboxyl oxygen atoms belonging to the carboxylate ligand with Ta-O distances ranging from

2.141(3) Å to 2.175(3) Å for compound **3** and from 2.132(3) Å to 2.183(3) Å for compound **4** ticle Online The Ta-O-Ta angles are about 144.9° and 149.5° for the concave and convex bending of compound **3** and about 144.7° and 150° for the concave and convex bending of compound **4**. Within the tetramers, the Ta-Ta bond lengths are in the range 3.664 Å - 3.669 Å for complex **3** and about 3.667 Å to 3.674 Å for complex **4**. In the lattice, the tetrameric units interact through σ - π stacking between the naphtoate ligands with distances of 2.876 Å and benzoate ligands with distances of 2.927 Å.



Figure 2. Structural representation of compound **3** and **4**; (a) Illustration of the tetranuclear core coordination environment (b) side view showing the relative position of the carboxylate ligands (isopropanolate groups have been removed for clarity).

Compound 5 [Ta₈(µ²-O)₁₂(L)₈(OiPr)₈]

This system crystallizes in the triclinic P-1 space group. The crystal structure of compound 5 is built up with eight tantalum centers, twelve bridging μ^2 -oxo groups, eight 2-naphtoate ligands and eight isopropanolate molecules. The cationic-oxo arrangement results in a cubic octanuclear core $\{Ta_8O_{12}\}$, where the tantalum atoms occupy the eight corners of a cube, and the bridging μ^2 -oxo groups are roughly located nearby the twelve edges (Figure 3a). This octanuclear arrangement can be viewed as the condensation of two tantalum-centered tetranuclear blocks through four additional μ^2 -oxo groups, located perpendicularly to its square plane of Ta-O-Ta bondings. In the octamer, four crystallographic inequivalent tantalum atoms labelled Ta1, Ta2, Ta3 and Ta4, are present. All of them are six-fold coordinated with the same kind of distorted octahedral geometry than in the previous molecular species described in the manuscript. The coordination sphere of each tantalum centers is composed of three μ^2 -oxo groups, two carboxyl oxygen atoms belonging to the 2-naphthoate ligand (in a bidentate synsyn bridging mode between two adjacent Ta) and one remaining oxygen atoms coming from one isopropanolate ligands (Figure 3b). The Ta-O_{oxo} bond distances are in the range 1.875(12) Å - 1.913(12) Å, whereas the Ta-O_{naphtoate} are longer and in the range 2.113(14) Å to 2.177(12) Å. The last Ta-O_{iPr} bond lengths (related to the isopropanolate) are observed in the range 1.854(11) Å to 1.913(12) Å. The Ta-O-Ta angles in the octanuclear compound are all convex

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and range from 146.5° to 150°. All the Ta-Ta bond distances in the molecular species are in the cle online range 3.639 Å to 3.669 Å as previously observed in the other dinuclear or tetranuclear compounds. The overall compound is also neutral. In each octanuclear species, the aromatic rings of the naphtoate ligands exhibit typical π - π interactions with average distances comprised between 3.598 Å and 3.719 Å for the four pairs of ligands. Interestingly, the eight ligands are located on both sides of the cubic {Ta₈O₁₂} arrangement in the (*b*,*c*) plane. The ligands from two distinct octamer also interact with weaker π - π stacking interactions with distances ranging from 3.591 Å and 3.632 Å. This tantalum octanuclear block as only been observed once in a related complex [Ta₈(O)₁₂(O₂CNEt₂)₁₆] stabilized by sixteen N,N-diethylcarbamato ligands acting either as monodentate or bidentate ligands and in a parent niobium compound described previously in our group.^{3,4}



Figure 3. Polyhedral representation of the molecular octanuclear coordination compound 5, $[Ta_8(\mu^2 - O)_{12}(C_{11}H_7O_2)_8(OiPr)_8]$.

Infrared spectroscopy and powder X-Ray Diffraction

All compounds were characterized by IR spectroscopy and PXRD (See Figures S2a-e and S3ab respectively). The powder X ray diffraction analysis shows that most of the crystalline phases of the five compounds contained the compounds described in the structure section. In addition, all the compounds are stable out of the mother liquor as we observe a good agreement (either in thickness and in band positions) between the experimental and theoretical diagrams calculated from the SC-XRD analyses in the figures S2.

The infrared measurements show that all compounds present characteristic vibrations related to the organic part, either the carboxylate or the isopropanolate ligands. As showed in Table 2, the

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carbonyl group of the free carboxylic acid ligands (located around 1680 cm⁻¹) disappear to the ligendate online benefit of classical $v_{asym(COO)}$ and $v_{sym(COO)}$ vibrations that lies around 1575-1602 cm⁻¹ and 1557-

1564 cm⁻¹ respectively. They clearly indicate the coordination of the ligands to the tantalum(V) centers through the carboxylate function.

We can also observe for compound **2**, on both PXRD and IR characterizations, the presence of several diffraction peaks and vibrations probably related to unreacted ligands as we have a characteristic $v_{C=O}$ vibration visible at 1687 cm⁻¹ for the compound spectrum. For unknow reason, modifying the ligand to tantalum ratio in several synthesis did not lead to the disappearance of the unreacted ligand.

		v(C=O) _{acid}	$v_{asym}(COO)$	$v_{sym}(COO)$
Compound 1	Compound 1 Anthracene-9-carboxylic		/	/
	acid			
	crystalline product	/	1575	1557
Compound 2	4'-methylbiphenyl-4-	1687	/	/
	carboxylic acid			
	crystalline product	/	1592	1564
Compound 3	benzoic acid	1680	/	/
	crystalline product	/	1602	1562
Compound 4	1-naphtoic acid	1668	/	/
	crystalline product	/	1599	1563
Compound 5	2-naphtoic acid	1682	/	/
	crystalline product	/	1591	1560

Table 2. Comparison of the v(C=O) vibrations (from the carboxylic acid function) and v(COO) vibrations (from the carboxylate function) for the complexes 1-5 (in cm⁻¹).

Structures discussion

The utilization of the various monocarboxylic ligands mentioned in the present work for the coordination of tantalum(V) centers, leads to the formation of several molecular species with nuclearities starting form a $\{Ta_2O\}$ dinuclear unit up to $\{Ta_4O_4\}$ tetranuclear units and a cubiclike {Ta₈O₁₂} octanuclear core. As previously described, these polynuclear species are obtained by the addition of several μ^2 -oxo bridges allowing, in the case of the tetranuclear and octanuclear species, the condensation of the classical dinuclear motif already present in the tantalum ethoxide precursor. The oxygen atoms allowing the condensation process to occur are not present on the initial reaction scheme as the synthesis are performed with great care, under a glove box with controlled atmosphere, to exclude the presence dioxygen and water. As previously described in the work performed in our team on niobium oxo-species,^{5,6} the emergence of these bridging atoms comes from an esterification reaction occurring between the alcohol ligands of the precursor and the carboxylic acid leading to the formation of an ester and water. This reaction can be of course transposed using the tantalum precursor: 2 x Ta-OEt + $H_2O \rightarrow Ta-O-Ta + 2 \times Et-OH$ and, the water formed in the esterification reaction is the source of oxygen necessary for the occurrence of the poly-condensation reaction. The crystalline phases of the five systems described in this work are pure with the exception of compound 2

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where, despite our efforts, the presence of supposedly unreacted ligands seems to be presenticle Online concomitantly with the dimer $[Ta_2(\mu^2-O)(C_{14}H_{11}O_2)_2(IprO)_6]$ itself.

It is worth noting a new observation revealed in this work, regarding the formation of polynuclear core of higher nuclearity. Indeed, the four compounds 1-4, including either dimeric or tetrameric tantalum oxo-cores are thoroughly synthesized using dry isopropanol solvent. However, the octanuclear moiety (compound 5) stabilized with 2-naphtoate ligands, was systematically obtained in high crystalline yields (up to 75%) using a mixture of solvents corresponding to "diluting" isopropanol with acetonitrile, the latter being a non-complexing species for this chemical system. The best crystallinity for SC-XRD purpose was obtained using a 9:1 molar ratio CH₃CN/iPrOH mixture, but the increase of the isopropanolate ratio up to 20% prevented the formation of the Ta-centered octanuclear complex. This behavior was not described in our previous work using 2-naphtoate ligands associated to niobium(V) cation as it was probably hidden by the synthetic procedure for obtaining the $\{Nb_8O_{12}\}$ core by using a large excess of ligands (12 equivalents per niobium centers).⁴ In our case, only three equivalents of 2-naphtoate ligands were necessary for the formation of the compound. One may assume the significant role played by the nature of the solvent in such synthesis. Isopropanol is a complexing solvent and probably enter in competition with the carboxylate ligands, thus preventing or limiting their coordination to the tantalum centers. Indeed, as can be seen in the three structural types, the alcoholate to carboxylate ligand ratio decrease from 3 to 2 down to 1 for the dimer, the tetramer and the octamer, respectively. Consequently, diminishing the isopropanol ratio in the solvent helps the coordination of the carboxylate ligands and the increase of the nuclearity without preventing the esterification reaction requested for the oxolation condensation process (μ_2 -O group bridging two adjacent tantalum centers). As expected, performing the synthesis in pure acetonitrile solvent did not lead to the formation of any crystalline material, probably because of the too low amount of alcohol species in the reaction medium preventing the beginning of the oxolation condensation reaction.

Another interesting point is that the same strategy using the other ligands mentioned in this work did not lead to the formation of an octanuclear species considering the diverse synthesis attempts that were done. It indicates a probable second effect with the bulky character of the monotopic linkers due to the presence of several aromatic rings in their structures generating more hindrance than the 2-naphtoate ligand. Regarding this specific ligand it is possible that the π - π stacking interactions observed and described in the molecular structure of the octameric compound plays an important role in the stability and formation of such crystalline molecular arrangement. In a purely speculative approach, with bulky ligands (anthracenoate, 4'-methylbiphenyl-4-carboxylic or 1-naphtoate) or the less bulky benzoate ligands, it may be more difficult to arrange the same π - π stacking interactions making the octanuclear cubic-like core more difficult to obtain in the appropriate solvent mixture.

Catalytic activity during the conversion of DiHydroxyAcetone (DHA)

The acido/basic properties of the compounds 1 (dinuclear Ta_2O core) and 5 (octanuclear Ta_8O_{12} core) were tested in aqueous media via the conversion of dihydroxyacetone (DHA) at 90 °C. Such reaction (Figure S5) is usually used to evaluate the Lewis/Brønsted acidity in water through the conversion of the DHA that produce lactic acid (LA) or/and pyruvaldehyde (PA).

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In the presence of basic sites, it could show production of sugars (C₆, such as glucostew of the online fructose). Figure 4 shows the evolution of the reaction as a function of the time observed using the compounds 1 & 5, as well as the DHA conversion and yield of the identified resulting products. By considering the same DHA/catalyst ratio of the used complexes (150 mg), the compound 1 shows higher kinetic for the conversion of DHA with 70% consumed in 6 hours compared to the 47% in the case of the compound 5. For both samples the observed products were PA, LA and sugars. The amount of each product obtained as a function of the DHA conversion can be seen in figure 4 (right), with about 50% of pyruvaldehyde formation and 5-10 % for lactic acid and C₆ sugars formation (based on %C).



Figure 4. DHA conversion (%) (left) and the identified resulting products (lactic acid (LA), pyruvaldehyde (PA) and C₆ sugars) for each test (right). Compound **1** (dinuclear Ta₂O core): lines; compound **5** (octanuclear Ta₈O₁₂ core): dash.

As expected, both compounds 1 & 5 exhibit acidic behavior with mostly Brønsted acid owing to the high yield of the pyruvaldehyde amount. The formation of lactic acid shows some Lewis sites in water alongside with C_6 sugars in few amounts. Since the tantalum(V) atoms are octahedrally coordinated to six oxygens, the presence of mostly Brønsted acidity agrees with the results already reported by Chen et al in the case of the inorganic compounds $Ta_2O_5 \cdot nH_2O$, for which a regular Ta-centered octahedral environment tends to exhibit Brønsted sites.⁵⁸ The benefit of the use of coordination polymers stable in water resides in the low concentration of used metallic centers and the possibility to tune the acidity of the catalysts.

Conclusion

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We have successfully obtain five molecular compounds 1-5 based on the complexation of the tantalum ethoxide Ta(OEt)₅ precursor by monocarboxylate ligands in isopropanol solvent. Three nuclearities were observed in this reactivity panel, dimeric, tetrameric and octameric entities with $\{Ta_2O\}$, $\{Ta_4O_4\}$ and $\{Ta_8O_{12}\}$ tantalum-oxo centers respectively. All these molecules have been characterized with various solid-state technics and appears to be stable out of the mother liquor with no visible degradation over several days. We observed the formation of the highest nuclearity (here $\{Ta_8O_{12}\}$ brick) when mixing the isopropanol with acetonitrile with a strict molar ratio of 1:9 (iPrOH:CH₃CN). It showed the influence of the balance of the complexing strength of the solvent (here IPrOH vs CH₃CN) towards the generation of higher nuclearity in the Ta-based complexes. This complexing behavior may be due to pKa differences between iPrOH/iPrO⁻ couple (17.1) and CH₃CN/CH₂CN⁻ couple (25) making the isopropanolate a much better complexing agent than acetonitrile. The geometry of these molecular moieties and peculiarly the cubic-like octanuclear core could be interesting to envision their use as building block for the formation of extended materials upon ligand substitution. We are currently investigating on the ligand exchanges possibilities in our research team. Preliminary catalytic tests (dihydroxyacetone conversion) on two selected compounds (1 & 5) indicated a Brønsted acid activity of compounds using Ta centers opening the way to multiple catalytic applications.

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Conflict of interests

The authors declare no conflict of interests.

Associated Content

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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 ¹H NMR and solid state ⁹³Nb spectra).

Accession Codes

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 2446460 for 1, 2446461 for 2, 2446462 for 3, 2446463 for 4, 2446464 for 5. 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-timailticle Online data_request@ccdc.cam.ac.uk).

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