



Cite this: *CrystEngComm*, 2025, 27, 4734

## Polynuclear tantalum(v) coordination complexes: from dinuclear $\{\text{Ta}_2\text{O}\}$ to octanuclear $\{\text{Ta}_8\text{O}_{12}\}$ oxo species connected through aryl monotopic carboxylate linkers†

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Received 25th April 2025,  
Accepted 1st June 2025

DOI: 10.1039/d5ce00444f

rsc.li/crystengcomm

### Introduction

Tantalum and niobium are known to be two closely related transition metals belonging to the same column (group 5) of the periodic table and have attracted a lot of attention in the past decades owing to their acidic catalytic properties in different fields of applications; the used materials are usually inorganic such as oxides, hydroxides, phosphates or MOFs.<sup>1</sup> 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.<sup>2,3</sup> 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) cations,<sup>4–7</sup> 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 into 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  $\text{Cp}^*$  ligand to form  $[\text{Cp}^*\text{TaCl}_4]$  precursors.  $\text{Cp}^*$  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-donor ligands to form mainly mononuclear compounds.<sup>8–19</sup> Following this route, some polynuclear entities were also obtained with the identification of the tri- and tetra-nuclear molecules  $[\{\text{TaCp}^*(\text{OH})(\text{OH}_2)\}_3(\mu^3\text{-OH})(\mu^2\text{-O})_3](\text{OTfH})_2$ ,  $[\{\text{Cp}^*\text{Ta}\}_4(\mu^3\text{-O})_7](\text{OH})_2$  and  $[\{\text{Cp}^*\text{Ta}\}_3(\mu^3\text{-O})_5\text{Cl}(\text{H}_2\text{O})_2]\text{Cl}$ .<sup>20–22</sup>

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† Electronic supplementary information (ESI) available: The data associated with the findings of this study can be found in the online version (optical microscopy photographs, powder XRD pattern, IR spectra, liquid  $^1\text{H}$  NMR and solid state  $^{93}\text{Nb}$  spectra). CCDC 2446460 for 1, 2446461 for 2, 2446462 for 3, 2446463 for 4, 2446464 for 5. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d5ce00444f>



Albeit being studied for 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.<sup>13,19</sup> Few other examples were also reported using N-heterocyclic carbene as the ligand for tantalum complexation with catalytic properties for cyclic carbonate formation<sup>23,24</sup> or incorporation of a carbon based electrophile to form a metal alkyl substrate or various compounds by additional reaction of the tantalum complex.<sup>25</sup> It is worth mentioning that for catalytic purposes, some tantalum hydride compounds were also described and used for carbon dioxide reduction reactions.<sup>26,27</sup> From a fundamental point of view, tantalum compounds presenting a unique coordination mode of dinitrogen were also described and further used for to react with propene or bromobenzyl.<sup>28</sup>

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<sup>V</sup>/Ta<sup>V</sup> separation,<sup>29</sup> the use of halide [MX<sub>5</sub>] compounds (M = Nb<sup>V</sup>, Ta<sup>V</sup>) for anhydride C-H activation reactions,<sup>30</sup> deposition of thin films of Ta<sub>2</sub>O<sub>5</sub> using the complex [Ta(NMe<sub>2</sub>)<sub>4</sub>(dmbl)] (dmbl = diterbutylmalonato)<sup>31</sup> and, in a more fundamental approach, discovering the coordination potentialities of the Ta(v) cation.<sup>32-38</sup>

Several mixed-metal compounds containing tantalum were obtained using oxalate (C<sub>2</sub>O<sub>4</sub>)<sup>2-</sup> or salicylate (O<sub>2</sub>C-C<sub>6</sub>H<sub>4</sub>-2-OH)<sup>-</sup> ligands. In these systems, the additive metallic cation (Bi, Ni) is either directly incorporated in the polynuclear core to form a {BiTa<sub>4</sub>O<sub>4</sub>} or {Bi<sub>2</sub>Ta<sub>2</sub>O} oxo-cluster,<sup>39-41</sup> or stand as a hybrid counter cation of [ML<sub>3</sub>]<sup>n+</sup> type (with L = phenanthroline or bipyridine) compensating for the negative charge of [TaO(C<sub>2</sub>O<sub>4</sub>)]<sup>3-</sup> complexes in the work of Dubraja *et al.*<sup>42-46</sup>

The literature related to the topic we developed and described 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<sub>2</sub>O} and tetranuclear {Ta<sub>4</sub>O<sub>4</sub>} moieties and a few octanuclear {Ta<sub>8</sub>O<sub>12</sub>} cores. Most of the reactions described in the literature were performed starting from non-common precursors such as mixed chloride-dimethylsulfide [Ta<sub>2</sub>Cl<sub>6</sub>(SMe<sub>2</sub>)<sub>3</sub>] and tetraperoxo-guanidinium tantalum [(gu)<sub>3</sub>Ta(O<sub>2</sub>)<sub>4</sub>] or the more classical pentachloro tantalum TaCl<sub>5</sub>. They gave rise to the isolation of dimeric entities with various carboxylate ligands, for instance {Ta<sup>III</sup><sub>2</sub>Cl<sub>5</sub>(piv)(SMe<sub>2</sub>)}

(THF)<sub>2</sub>} with piv = pivalate,<sup>47</sup> {Ta<sub>2</sub>(O<sub>2</sub>)<sub>4</sub>(tart)<sub>2</sub>} with tart = tartrate,<sup>48</sup> {Ta<sub>2</sub>Cl<sub>8</sub>(p-Cl-benz)} with p-Cl-benz = p-chlorobenzoate<sup>49</sup> and {Ta<sub>2</sub>(lactate)<sub>4</sub>(O<sub>2</sub>)<sub>2</sub>O} with lactate<sup>50</sup> or with some other ligands.<sup>51,52</sup>

Tetranuclear species like {Ta<sub>4</sub>(μ-O)<sub>4</sub>(μ-OBc)<sub>4</sub>(ONep)<sub>8</sub>}<sup>52</sup> or {Ta<sub>4</sub>(μ-O)<sub>4</sub>Cl<sub>8</sub>(p-Mebenzoate)<sub>4</sub>}<sup>53</sup> were also synthetized using more bulky carboxylate ligands (OBc = pivalate and p-Mebenzoate = *para*-methylbenzoate), eventually associated with alkoxide molecules (ONep = 2,2-dimethylpropan-1-olate) using standard solution synthesis. In these cases, the bulky nature of the ligands was reported as being the main driving force of the increase in nuclearity of the tantalum-oxo core. Another tetranuclear compound with applications in ring opening polymerization was described using the bifunctional (carboxylate and alcoholate) benzyllic acid ligand.<sup>51</sup>

Finally, in the race to obtain large clusters, the first octanuclear tantalum compound {Ta<sub>8</sub>(μ-O)<sub>12</sub>(O<sub>2</sub>CNET<sub>2</sub>)<sub>16</sub>} (O<sub>2</sub>-CNET<sub>2</sub> = diethyl carbamate) was structurally characterized by Pampaloni *et al.* in 1998. It remains the only illustration in tantalum “hybrid” chemistry up to date.<sup>3</sup>

Herein we report on new results obtained by using five aromatic monocarboxylic acid ligands to investigate their reactivity towards the tantalum penta-ethoxide Ta(OEt)<sub>5</sub> precursor as the tantalum(v) metal source and generating diverse Ta-centered nuclearities. Anthracene-9-carboxylic acid and 4'-methylbiphenyl-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 the 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)<sub>5</sub>, 99%, Thermo Fisher), benzoic acid (C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>, 99.5%, Sigma Aldrich), 1-naphtoic acid (C<sub>11</sub>H<sub>8</sub>O<sub>2</sub>, 96%, Sigma Aldrich), 2-naphtoic acid (C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>, 98%, Sigma Aldrich), 4'-methylbiphenyl-4-carboxylic acid (C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>, 96%, Sigma Aldrich), anthracene-9-carboxylic acid (C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>, 99%, Sigma Aldrich), anhydrous isopropanol (C<sub>3</sub>H<sub>8</sub>O, 99.5%, Sigma Aldrich), anhydrous acetonitrile (C<sub>4</sub>H<sub>3</sub>N, 99.8%, Thermo Fisher). The chemical reactants were commercially available and 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 with regard to moisture, all synthesis mixtures were prepared in a glovebox using dried solids and extra dried isopropanol (iPrOH) or acetonitrile (CH<sub>3</sub>CN) solvent. 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 gave rise to the identification of five crystalline materials with single crystal solids of sufficient quality (Fig. S1†) for performing single crystal X-ray diffraction (SC-XRD) analyses.

#### Compound 1 $[(\text{Ta}_2(\mu\text{-O})(\text{O}i\text{Pr})_6)(\text{C}_{15}\text{H}_9\text{O}_2)_2]$

A mixture of 3.5  $\mu\text{L}$  (0.013 mmol) Ta(OEt)<sub>5</sub> 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 (Fig. S1†). Compound 1 was analyzed by optical and scanning electron microscopy showing large plate-shaped crystals up to 300  $\mu\text{m}$  in size. The resulting crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 88.3%<sub>Ta</sub>.

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

#### Compound 2 $[(\text{Ta}_2(\mu\text{-O})(\text{O}i\text{Pr})_6)(\text{C}_{14}\text{H}_{11}\text{O}_2)_2]$

A mixture of 3.5  $\mu\text{L}$  (0.013 mmol) Ta(OEt)<sub>5</sub> 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 (Fig. S1†). Compound 2 was analyzed by optical microscopy showing parallelepiped-shape crystals up to 150  $\mu\text{m}$  in size. The resulting crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 12.8%<sub>Ta</sub>.

#### Compound 3 $[\text{Ta}_4(\mu\text{-O})_4(\text{O}i\text{Pr})_8(\text{C}_7\text{H}_5\text{O}_2)_4]$

A mixture of 3.5  $\mu\text{L}$  (0.013 mmol) Ta(OEt)<sub>5</sub> 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 (Fig. S1†). Compound 3 was analyzed by optical microscopy showing plate-shaped crystals up to 400  $\mu\text{m}$  in size. The resulting yellowish crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 17.3%<sub>Ta</sub>.

Elemental analyses: C (35.2%), H (4.2%). Calc. C (35.8%), H (4.36%).

#### Compound 4 $[\text{Ta}_4(\mu\text{-O})_4(\text{O}i\text{Pr})_8(\text{C}_{11}\text{H}_7\text{O}_2)_4]$

A mixture of 3.5  $\mu\text{L}$  (0.013 mmol) Ta(OEt)<sub>5</sub> 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 (Fig. S1†). Compound 4 was analyzed by optical microscopy showing square block crystals up to 150  $\mu\text{m}$  size. The resulting yellowish crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 68.3%<sub>Ta</sub>.

Elemental analyses: C (42.2%), H (4.2%). Calc. C (42.0%), H (4.3%).

#### Compound 5 $[(\text{Ta}_8(\mu\text{-O})_{12}(\text{O}i\text{Pr})_8)(\text{C}_{11}\text{H}_7\text{O}_2)_8]$

A mixture of 3.5  $\mu\text{L}$  (0.013 mmol) Ta(OEt)<sub>5</sub> 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 (Fig. S1†). Compound 5 was analyzed by optical microscopy showing parallelepiped crystals up to 400  $\mu\text{m}$  in size. The resulting yellowish crystals were filtered off, washed with ethanol and dried at room temperature. Crystallization yield was 75.3%<sub>Ta</sub>.

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

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

#### Single-crystal X-ray diffraction

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

Data reduction was accomplished using SAINT V8.34a.<sup>54</sup> 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.<sup>55</sup> 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,<sup>56</sup> implemented in the OLEX2 graphical tool.<sup>57</sup>

The crystal data are given in Table 1. The ESI† 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 ESI† crystallographic data for this paper.



**Table 1** Crystal data and structure refinements for compounds **1–5**

	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Formula	$C_{48}H_{60}Ta_2O_{11}$	$C_{46}H_{64}Ta_2O_{11}$	$C_{52}H_{76}Ta_4O_{20}$	$C_{68}H_{24}Ta_4O_{20}$	$C_{112}H_{110}Ta_8O_{36}$
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	$0.15 \times 0.12 \times 0.02$	$0.227 \times 0.086 \times 0.075$	$0.121 \times 0.118 \times 0.087$	$0.206 \times 0.085 \times 0.078$	$0.27 \times 0.13 \times 0.12$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$C2/c$	$C2/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$
$a/\text{\AA}$	22.0631(12)	24.6357(5)	11.9823(9)	14.4485(8)	11.3938(14)
$b/\text{\AA}$	10.1086(4)	9.2183(2)	18.5216(15)	12.6909(7)	23.187(4)
$c/\text{\AA}$	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)
$\gamma/^\circ$	90	90	90	90	80.786(5)
Volume/ $\text{\AA}^3$	4835.6(4)	4802.90(18)	3185.3(4)	3622.8(3)	6218.8(17)
$Z, \rho_{\text{calculated}}/\text{g cm}^{-3}$	4, 1.614	4, 1.597	2, 1.819	2, 1.783	1, 1.859
$\mu/\text{mm}^{-1}$	2.465	4.608	3.717	3.275	3.806
$\theta$ range/ $^\circ$	2.711–20.551	1.926–26.382	2.065–23.638	2.526–21.982	0.674–20.702
Limiting indices	$-27 \leq h \leq 27$ $-12 \leq k \leq 12$ $-27 \leq l \leq 27$	$-30 \leq h \leq 30$ $-11 \leq k \leq 11$ $-26 \leq l \leq 26$	$-17 \leq h \leq 16$ $-26 \leq k \leq 26$ $-20 \leq l \leq 19$	$-19 \leq h \leq 19$ $-16 \leq k \leq 16$ $-26 \leq l \leq 27$	$-13 \leq h \leq 14$ $-29 \leq k \leq 29$ $-30 \leq l \leq 30$
Collected reflections	70 322	61 939	100 994	116 530	339 380
Unique reflections	4952	4922	9720	8972	25 543
Parameters	[ $R(\text{int}) = 0.0777$ ]	[ $R(\text{int}) = 0.0496$ ]	[ $R(\text{int}) = 0.0407$ ]	[ $R(\text{int}) = 0.0608$ ]	[ $R(\text{int}) = 0.0725$ ]
Goodness-of-fit on $F^2$	1.092	1.082	1.166	1.220	1.116
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0281$ $wR_2 = 0.0544$	$R_1 = 0.0346$ $wR_2 = 0.0661$	$R_1 = 0.0262$ $wR_2 = 0.0461$	$R_1 = 0.0279$ $wR_2 = 0.0531$	$R_1 = 0.0766$ $wR_2 = 0.1469$
$R$ indices (all data)	$R_1 = 0.0447$ $wR_2 = 0.0628$	$R_1 = 0.0496$ $wR_2 = 0.0690$	$R_1 = 0.0428$ $wR_2 = 0.0559$	$R_1 = 0.0462$ $wR_2 = 0.0635$	$R_1 = 0.1258$ $wR_2 = 0.1907$
Largest diff. peak and hole/e $\text{\AA}^{-3}$	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

### 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 ( $H_2SO_4$  1.7 mM) was used as the mobile phase (0.6 mL min<sup>-1</sup>). 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.

### Powder X-ray diffraction

X-ray powder diffraction was performed on a Bruker D8 Advance diffractometer (LynxEye detector) in a Bragg-Brentano  $\theta$ - $\theta$  mode using Cu-K $\alpha$  radiation. Each powder pattern was recorded within an angular range of 5–50° in  $2\theta$ , 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 (accelerating voltage = 5 kV, secondary electron mode, working distance = 5.3 to 5.5 mm).

**IR spectroscopy.** Infrared spectra were measured on a Perkin Elmer Spectrum Two™ spectrometer between 4000 and 400  $\text{cm}^{-1}$ , 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<sup>-1</sup>.

## Results and discussion

### Structure description

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-naphthoic acid crystallize as tetramers with



$\{\text{Ta}_4\text{O}_4\}$  moieties and compound **5** with 2-naphtoic acid is obtained as an octamer with a  $\{\text{Ta}_8\text{O}_{12}\}$  core.

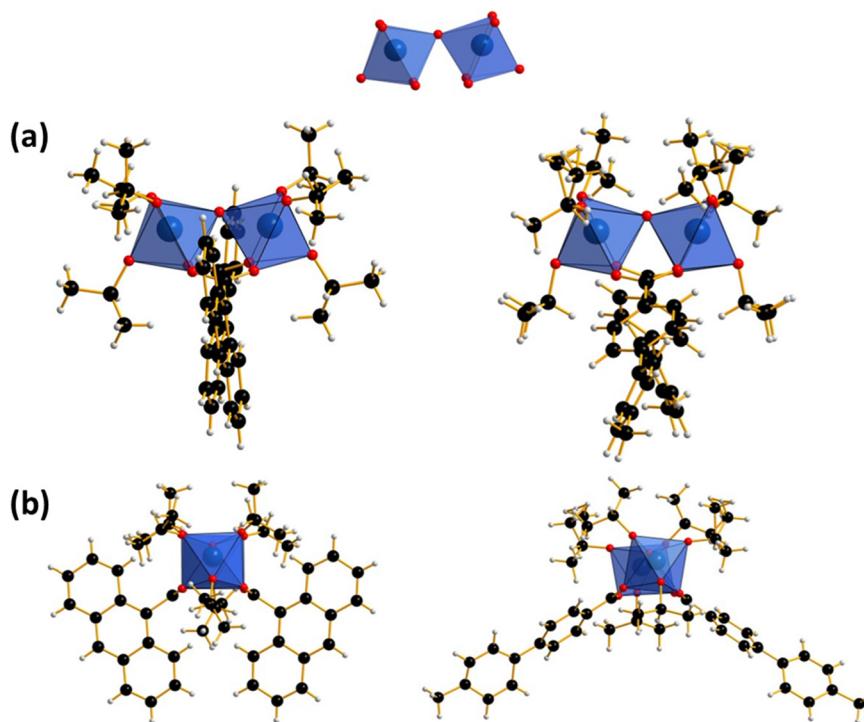
### Compounds **1** and **2** of the general formula type $[\text{Ta}_2(\mu^2\text{-O})(\text{L})_2(\text{O}i\text{Pr})_6]$

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 from 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 dimeric  $\{\text{Ta}_2\text{O}\}$  moieties surrounded by a total of two carboxylate and six isopropanolate ligands (Fig. 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  $\text{Ta}-\text{O}i\text{Pr}$  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 ( $\text{Ta}-\text{O} = 2.163(3)$  Å and  $\text{Ta}-\text{O} = 2.207(3)$  Å) for compound **1** and ( $\text{Ta}-\text{O} = 2.146(3)$  Å and  $\text{Ta}-\text{O} = 2.178(3)$  Å) for compound **2**. Finally, the coordination sphere of both tantalum atoms is completed by one oxygen atom bridging the two centers

together with  $\text{Ta}-\text{O}$  distances of  $1.9133(12)$  Å for compound **1** and  $1.9221(14)$  Å for compound **2**. The  $\text{Ta1-Ta1}$  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-9-carboxylate 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  $\{\text{Ta}_2\text{O}\}$  unit with a  $\text{Ta1-O1-Ta1}$  angle of about  $145.7^\circ$ .

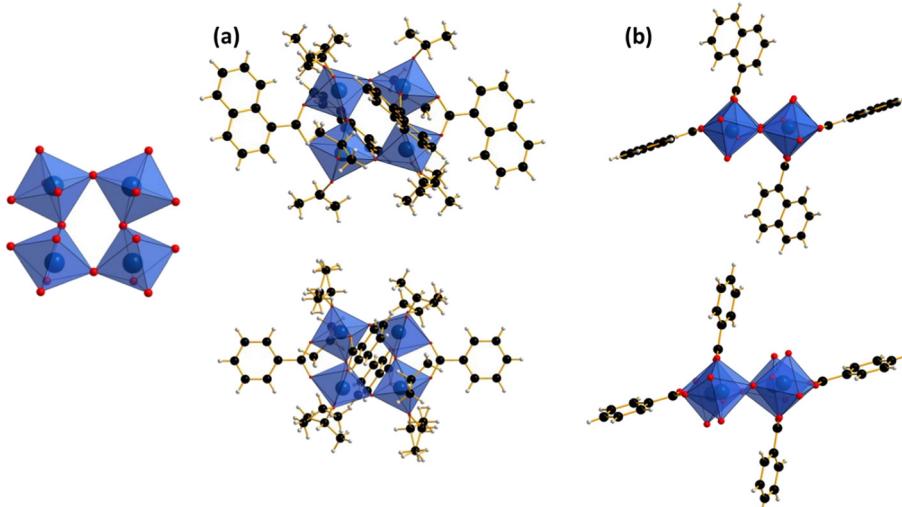
### Compounds **3** and **4** of the general formula type $[\text{Ta}_4(\mu^2\text{-O})_4(\text{L})_4(\text{O}i\text{Pr})_8]$

Both compounds crystallize 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  $\{\text{Ta}_4\text{O}_4\}$  motif stabilized either by benzoate or 1-naphtoate ligands and further decorated by eight isopropanolate groups (Fig. 2). They are built up from two crystallographically inequivalent tantalum(v) atoms, Ta1 and Ta2, linked to each other *via*  $\mu^2$ -oxo groups, within a square-ring unit (Fig. 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  $\mu^2$ -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



**Fig. 1** Structural representation of compounds **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.

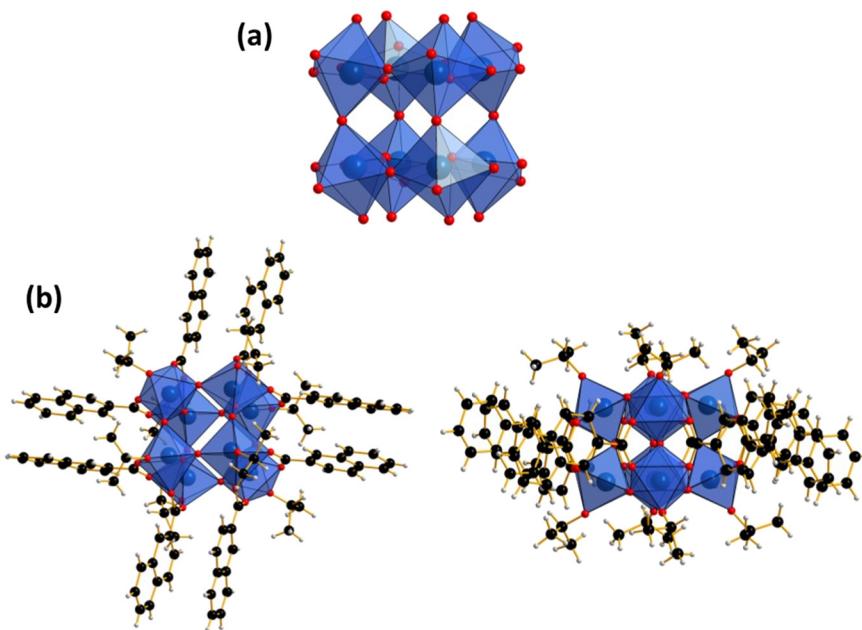




**Fig. 2** Structural representation of compounds **3** and **4**; (a) illustration of the tetranuclear core coordination environment and (b) side view showing the relative position of the carboxylate ligands (isopropanolate groups have been removed for clarity).

the two others are located above and under this plane (see Fig. 2b). Each tantalum center of complexes **3** and **4** is in a six-fold coordination oxo environment with a distorted octahedral geometry. The tantalum cations are surrounded by two  $\mu^2$ -oxo groups with Ta–O distances 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**. 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 3.664–3.669 Å for complex **3** and about 3.667 Å to 3.674 Å for complex **4**. In the lattice, the tetrameric units interact through  $\sigma$ – $\pi$  stacking between the naphthoate ligands with distances of 2.876 Å and benzoate ligands with distances of 2.927 Å.



**Fig. 3** Polyhedral representation of the molecular octanuclear coordination compound **5**,  $[\text{Ta}_8(\mu\text{-O})_{12}(\text{O}i\text{Pr})_8(\text{C}_{11}\text{H}_7\text{O}_2)_8]$ . (a) Nb-oxo core cluster and (b) top and side view of the complete octanuclear compound.



**Compound 5**  $[\text{Ta}_8(\mu^2\text{-O})_{12}(\text{L})_8(\text{O}i\text{Pr})_8]$ 

This system crystallizes in the triclinic  $P\bar{1}$  space group. The crystal structure of compound 5 is built up with eight tantalum centers, twelve bridging  $\mu^2$ -oxo groups, eight 2-naphthoate ligands and eight isopropanolate molecules. The cationic-oxo arrangement results in a cubic octanuclear core  $\{\text{Ta}_8\text{O}_{12}\}$ , where the tantalum atoms occupy the eight corners of a cube, and the bridging  $\mu^2$ -oxo groups are roughly located nearby the twelve edges (Fig. 3a). This octanuclear arrangement can be viewed as the condensation of two tantalum-centered tetranuclear blocks through four additional  $\mu^2$ -oxo groups, located perpendicularly to its square plane of  $\text{Ta}-\text{O}-\text{Ta}$  bonds. In the octamer, four crystallographic inequivalent tantalum atoms labelled  $\text{Ta}1$ ,  $\text{Ta}2$ ,  $\text{Ta}3$  and  $\text{Ta}4$  are present. All of them are six-fold coordinated with the same kind of distorted octahedral geometry as in the previous molecular species described in the manuscript. The coordination sphere of each tantalum center is composed of three  $\mu^2$ -oxo groups, two carboxyl oxygen atoms belonging to the 2-naphthoate ligand (in a bidentate *syn-syn* bridging mode between two adjacent Ta) and one remaining oxygen atom coming from one isopropanolate ligand (Fig. 3b). The  $\text{Ta}-\text{O}_{\text{oxo}}$  bond distances are in the range of 1.875(12)–1.913(12) Å, whereas the  $\text{Ta}-\text{O}_{\text{naphthoate}}$  bonds are longer and in the range of 2.113(14) Å to 2.177(12) Å. The last  $\text{Ta}-\text{O}_{i\text{Pr}}$  bond lengths (related to the isopropanolate) are observed in the range of 1.854(11) Å to 1.913(12) Å. The  $\text{Ta}-\text{O}-\text{Ta}$  angles in the octanuclear compound are all convex and range from 146.5° to 150°. All the  $\text{Ta}-\text{Ta}$  bond distances in the molecular species are in the range of 3.639 Å to 3.669 Å as previously observed in other dinuclear or tetranuclear compounds. The overall compound is also neutral. In each octanuclear species, the aromatic rings of the naphthoate ligands exhibit typical  $\pi-\pi$  interactions with average distances 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  $\{\text{Ta}_8\text{O}_{12}\}$  arrangement in the (b, c) plane. The ligands from two distinct octamers also interact with weaker  $\pi-\pi$  stacking interactions with distances ranging from 3.591 Å and 3.632 Å. This tantalum octanuclear block has only

been observed once in a related complex  $[\text{Ta}_8(\text{O})_{12}(\text{O}_2\text{-CNET}_2)_{16}]$  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.<sup>3,4</sup>

**Infrared spectroscopy and powder X-ray diffraction**

All the compounds were characterized by IR spectroscopy and PXRD (see Fig. S2a–e, S3a and b† 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 Fig. S2.†

The infrared measurements show that all the compounds present characteristic vibrations related to the organic part, either the carboxylate or the isopropanolate ligands. As shown in Table 2, the carbonyl group of the free carboxylic acid ligands (located around 1680  $\text{cm}^{-1}$ ) disappears to the benefit of classical  $\nu_{\text{asym}}(\text{COO})$  and  $\nu_{\text{sym}}(\text{COO})$  vibrations that lie around 1575–1602  $\text{cm}^{-1}$  and 1557–1564  $\text{cm}^{-1}$  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  $\nu_{\text{C=O}}$  vibration visible at 1687  $\text{cm}^{-1}$  for the compound spectrum. For unknown reasons, modifying the ligand to tantalum ratio in several syntheses did not lead to the disappearance of the unreacted ligand.

**Structure 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 from a  $\{\text{Ta}_2\text{O}\}$  dinuclear unit up to  $\{\text{Ta}_4\text{O}_4\}$  tetranuclear units and a cubic-like  $\{\text{Ta}_8\text{O}_{12}\}$  octanuclear core. As previously described, these polynuclear species are obtained by the addition of several  $\mu^2$ -oxo bridges allowing, in the case of the tetranuclear and

**Table 2** Comparison of the  $\nu(\text{C=O})$  vibrations (from the carboxylic acid function) and  $\nu(\text{COO})$  vibrations (from the carboxylate function) for complexes 1–5 (in  $\text{cm}^{-1}$ )

		$\nu(\text{C=O})_{\text{acid}}$	$\nu_{\text{asym}}(\text{COO})$	$\nu_{\text{sym}}(\text{COO})$
Compound 1	Anthracene-9-carboxylic acid Crystalline product	1674 —	— 1575	— 1557
Compound 2	4'-Methylbiphenyl-4-carboxylic acid Crystalline product	1687 —	— 1592	— 1564
Compound 3	Benzoic acid Crystalline product	1680 —	— 1602	— 1562
Compound 4	1-Naphthoic acid Crystalline product	1668 —	— 1599	— 1563
Compound 5	2-Naphthoic acid Crystalline product	1682 —	— 1591	— 1560



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 is performed with great care, in 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,<sup>5,6</sup> 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:  $2 \times \text{Ta-OEt} + \text{H}_2\text{O} \rightarrow \text{Ta-O-Ta} + 2 \times \text{Et-OH}$ , 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 where, despite our efforts, the presence of supposedly unreacted ligands seems to be present concomitantly with the dimer  $[\text{Ta}_2(\mu^2-\text{O})(\text{C}_{14}\text{H}_{11}\text{O}_2)_2(\text{iPrO})_6]$  itself.

It is worth noting that there is a new observation revealed in this work, regarding the formation of a 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-naphthoate ligands, was systematically obtained in high crystalline yield (up to 75%) using a mixture of solvents corresponding to “diluting” isopropanol with acetonitrile, with the latter being a non-complexing species for this chemical system. The best crystallinity for SC-XRD purposes was obtained using a 9:1 molar ratio of the  $\text{CH}_3\text{CN}/\text{iPrOH}$  mixture, but the increase of the isopropanol ratio up to 20% prevented the formation of the Ta-centered octanuclear complex. This behavior was not described in our previous work using 2-naphthoate ligands associated with the niobium(v) cation as it was probably hidden by the synthetic procedure for obtaining the  $\{\text{Nb}_8\text{O}_{12}\}$  core by using a large excess of ligands (12 equivalents per niobium centers).<sup>4</sup> In our case, only three equivalents of 2-naphthoate 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 competes 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 decreased 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 required for the oxolation condensation process ( $\mu_2\text{O}$  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.

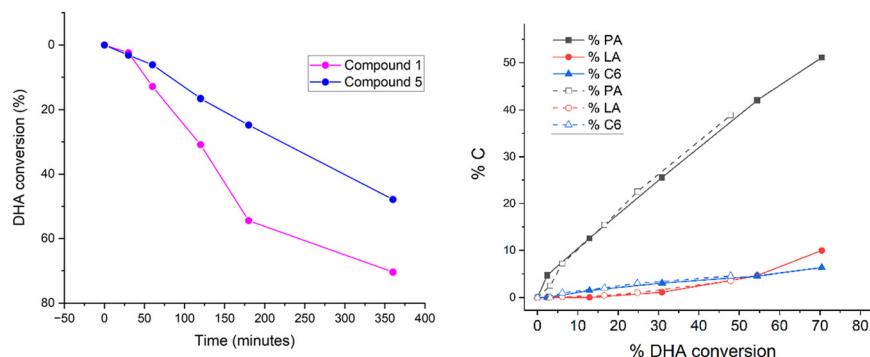
Another interesting point is that the same strategy using the other ligands mentioned in this work did not lead to the formation of an octanuclear species considering the diverse synthesis attempts that were done. It indicates a probable second effect with the bulky character of the monotopic linkers due to the presence of several aromatic rings in their structures generating more hindrance than the 2-naphthoate ligand. Regarding this specific ligand it is possible that the  $\pi-\pi$  stacking interaction observed and described in the molecular structure of the octameric compound plays an important role in the stability and formation of such a crystalline molecular arrangement. In a purely speculative approach, with bulky ligands (anthracenoate, 4'-methylbiphenyl-4-carboxylic or 1-naphthoate) or the less bulky benzoate ligands, it may be more difficult to arrange the same  $\pi-\pi$  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 compounds **1** (dinuclear  $\text{Ta}_2\text{O}$  core) and **5** (octanuclear  $\text{Ta}_8\text{O}_{12}$  core) were tested in aqueous media *via* the conversion of dihydroxyacetone (DHA) at 90 °C. Such a reaction (Fig. S5†) is usually used to evaluate the Lewis/Brønsted acidity in water through the conversion of DHA that produces lactic acid (LA) or/and pyruvaldehyde (PA). In the presence of basic sites, it could show production of sugars ( $\text{C}_6$ , such as glucose or fructose). Fig. 4 shows the evolution of the reaction as a function of the time observed using 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), compound **1** shows higher kinetics for the conversion of DHA with 70% consumed in 6 hours compared to 47% in the case of 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 Fig. 4 (right), with about 50% pyruvaldehyde formation and 5–10% for lactic acid and  $\text{C}_6$  sugar formation (based on %C).

As expected, both compounds **1** & **5** exhibit acidic behavior with mostly Brønsted acid owing to the high yield of pyruvaldehyde. The formation of lactic acid shows some Lewis sites in water alongside with  $\text{C}_6$  sugars in small amounts. Since the tantalum(v) atoms are octahedrally coordinated to six oxygens, the presence of mostly Brønsted acid sites agrees with the results already reported by Chen *et al.* in the case of the inorganic compounds  $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , for which a regular Ta-centered octahedral environment tends to exhibit Brønsted sites.<sup>58</sup> 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.





**Fig. 4** DHA conversion (%) (left) and the identified resulting products (lactic acid (LA), pyruvaldehyde (PA) and C<sub>6</sub> sugars) for each test (right). Compound 1 (dinuclear Ta<sub>2</sub>O core): lines; compound 5 (octanuclear Ta<sub>8</sub>O<sub>12</sub> core): dash.

## Conclusion

We have successfully obtained five molecular compounds **1–5** based on the complexation of the tantalum ethoxide Ta(OEt)<sub>5</sub> precursor with monocarboxylate ligands in isopropanol solvent. Three nuclearities were observed in this reactivity panel, dimeric, tetrameric and octameric entities with {Ta<sub>2</sub>O}, {Ta<sub>4</sub>O<sub>4</sub>} and {Ta<sub>8</sub>O<sub>12</sub>} tantalum-oxo centers, respectively. All these molecules have been characterized with various solid-state techniques and appear 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<sub>8</sub>O<sub>12</sub>} brick) when mixing isopropanol with acetonitrile with a strict molar ratio of 1:9 (iPrOH:CH<sub>3</sub>CN). It showed the influence of the balance of the complexing strength of the solvent (here iPrOH vs. CH<sub>3</sub>CN) on the generation of higher nuclearity in the Ta-based complexes. This complexing behavior may be due to pK<sub>a</sub> differences between the iPrOH/iPrO<sup>−</sup> couple (17.1) and CH<sub>3</sub>CN/CH<sub>2</sub>CN<sup>−</sup> couple (25) making isopropanolate a much better complexing agent than acetonitrile. The geometry of these molecular moieties and the peculiar cubic-like octanuclear core could be interesting to use as building blocks for the formation of extended materials upon ligand substitution. We are currently investigating the ligand exchange 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.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

The authors declare no conflict of interests.

## Acknowledgements

The authors would like to thank Mrs. Laurence Burylo, Mr. Rémi Lamblin and Mr. Philippe Devaux for their assistance with

the synthesis, SEM images, and XRD powder pattern measurements (UCCS). The “Fonds Européen de Développement Régional (FEDER)”, “CNRS”, “Région Hauts de France” and “Ministère de l’Education Nationale de l’Enseignement Supérieur et de la Recherche” are acknowledged for the funding of X-ray diffractometers and ICP-AES apparatus from the Chevreul Institute platform. The catalytic tests were supported by the France 2030 framework under the PEPRI DIADEM (DREAM-BIO, project ANR-23-PEXD-0007).

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